OCTOBER - DECEMBER • 1955

VOLUME XXVIII • NUMBER FOUR

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

KOSMOS 60

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil, and its manufacture is scientifically controlled to meet the highest standards. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

Charleston 27, W. Va.

New York • Akron • Chicago • Boston • Memphis

Canada: Canadian Industries (1954) Limited.

PHILBLACK® EXPERIENCE with tires

covers many years and millions of miles!

We've tested tires on the road and in the laboratory. We've timed the rate of growth of cuts and cracks. We've measured the treads to a thousandth of an inch to find the abrasion rate. And we've compiled important data on flex life, aging, and tensile strength.

From this information we've developed rubber recipes best suited for particular needs . . . for tough, low-cost tire carcasses, for longer-wearing treads and for other applications.

If you have a special problem our Philblack research department may have the solution. If not, we'll try to get the answer for you. For information consult your Philblack technical representative.

Meet the Philblacks!

KNOW WHAT THEY'LL DO FOR YOU!

A — **Philblack A FEF Fast Extrusion Furnace Black**
Ideal for smooth tubing, accurate molding, satiny finish. Mixes easily. High, hot tensile. Disperses heat. Non-staining.

I — **Philblack I ISAF Intermediate Super Abrasion Furnace Black**
Superior abrasion resistance at moderate cost. Very high resistance to cuts and cracks. More tread miles at high speeds.

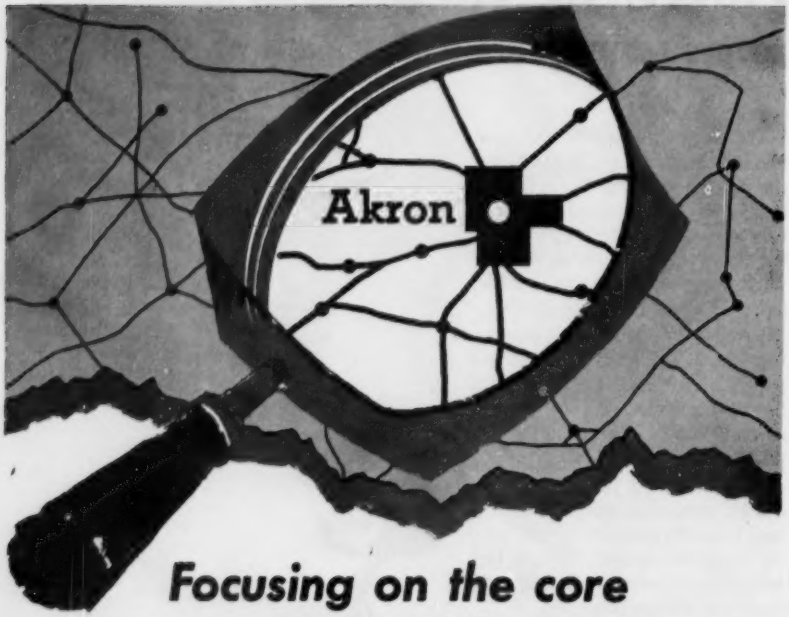
O — **Philblack O HAF High Abrasion Furnace Black**
For long, durable life. Good electrical conductivity. Excellent flex. Fine dispersion.

E — **Philblack E SAF Super Abrasion Furnace Black**
Toughest black on the market. Extreme abrasion resistance. Withstands aging, cracking, cutting and chipping.

Phillips 66

PHILLIPS CHEMICAL COMPANY, Rubber Chemicals Division, 318 Water St., Akron 8, Ohio.
Export Sales: 80 Broadway, New York 5, N. Y.
West Coast: Harwick Standard Chemical Company, Los Angeles, California.

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.



Focusing on the core of the RUBBER INDUSTRY

New WITCO-CONTINENTAL sales office and technical service laboratory at 213 West Bowery Street, AKRON, OHIO.

Operating modern and complete technical service facilities in this location, Witco-Continental now provides quicker, more efficient service to the rubber industry.

Our technical service staff will be glad to assist you with your rubber formulations. For Witco-Continental service in the Akron area, call POrtage 2-8881 – in Cleveland call CHerry 1-0583 – or call the Witco sales office nearest you.

WITCO *35 Years of Growth*

WITCO CHEMICAL COMPANY
CONTINENTAL CARBON COMPANY

122 East 42nd Street, New York 17, N. Y.

Chicago • Boston • Akron-Cleveland • Atlanta • Houston • Amarillo
Los Angeles • San Francisco • London and Manchester, England

DOUBLE-CHECKED ✓ CHEMICALS FOR THE RUBBER INDUSTRY

MERAC

A LIQUID ACCELERATOR FOR LATEX— NATURAL and SYNTHETIC

✓ SIMPLIFIES LATEX COMPOUNDING

✓ ADD DIRECTLY TO LATEX

✓ NO GRINDING OR BALL MILLING NECESSARY

Merac Offers these Advantages:

1. It is a liquid accelerator which upon dilution with water is added directly to latex.
2. It is faster curing at room and elevated curing temperatures than most accelerators.
3. It imparts high modulus and tensile strength with flat curing and good aging characteristics.
4. Its use provides compounded latex formulations which are stable on storage, exhibiting only moderate changes in viscosity.

PROPERTIES

Color—	Deep red to brown
Odor—	Characteristic
Sp. Gr.—	1.034 at 20°C.

Soluble in water

For technical information write to

✓ Pennsalt Chemicals

SHARPLES CHEMICALS Division

PENNSYLVANIA SALT MANUFACTURING COMPANY

500 Fifth Ave., New York • 80 E. Jackson Boulevard, Chicago • 106 S. Main St., Akron

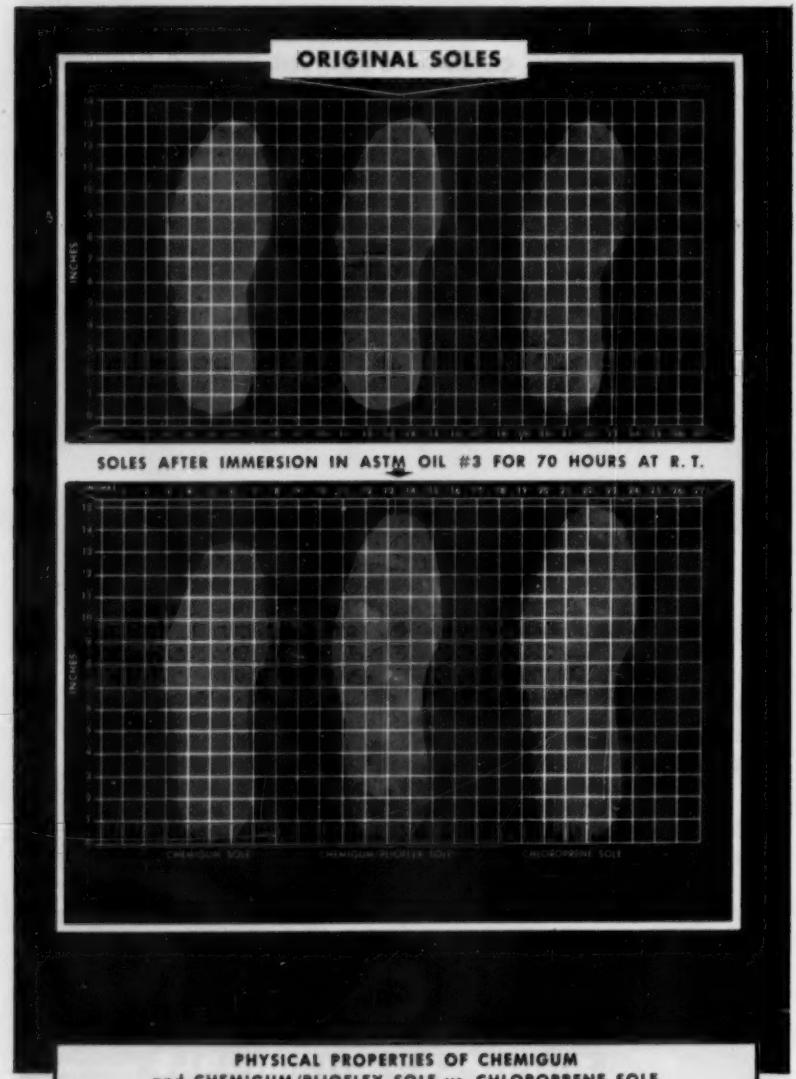
Executive Offices: Philadelphia, Pa.

Martin, Hoyt & Milne Inc., San Francisco • Los Angeles • Seattle • Portland

Shawinigan Chemicals, Ltd., Montreal • Toronto

Airco Company International, New York

CHEMIGUM . . . another quality product of Goodyear Chemical Division



PHYSICAL PROPERTIES OF CHEMIGUM and CHEMIGUM/PLIOFLEX SOLE vs. CHLOROPRENE SOLE

	HARDNESS (SHORE A)	CRESCENT TEAR, LBS./IN.	ROSS FLEX (12 HOUR SOLE AGED 24 HRS. @ 212°F.— ASTM #1 OIL AGED 70 HRS. @ 121°F.)	ABRASION RESISTANCE (BUREAU OF STANDARDS)	VOLUME SWELL, % INCREASE (AGED 70 HRS. IN ASTM #3 OIL @ 158°F.)	SPECIFIC GRAVITY	COST/LB. VOL.
CHEMIGUM SOLE*	86	521	43,238	90.7	3.66	1.305	41.3¢
CHEMIGUM/PLIOFLEX SOLE*	83	288	87,285	53.8	44.4	1.298	36.3¢
CHLOROPRENE SOLE*	90	416	47,008	56.6	71.2	1.42	40.7¢

*Formulations available on request

A NEW TREND UNDERFOOT

—and the key is CHEMIGUM

Here's something new for shoe soles or any other rubber product where oil resistance may be needed. It's a series of stocks based on blends of CHEMIGUM and PLIOFLEX.

CHEMIGUM is the easy processing nitrile – first and finest of its type in the field. PLIOFLEX is a styrene rubber of the highest quality. Both have been used individually in high-grade shoe soles of various types.

Now, these outstanding rubbers have been blended to provide sole stocks which are better in combined oil-resistance and general performance properties than those provided by other types of rubber or blends (see photos and table). Other distinct advantages are a low specific gravity for a lighter weight sole at a very attractive pound-volume cost and excellent low temperature properties.

Moreover, you'll find these CHEMIGUM/PLIOFLEX blends are easy to process. They exhibit excellent bin aging properties, safe scorch values and can be mixed in the same manner as straight styrene rubber stocks. That's because CHEMIGUM, like PLIOFLEX, tends to soften under mastication.

Why not learn more about high-quality, low-cost CHEMIGUM/PLIOFLEX blends for shoe soles, hose, belting, molded goods or any rubber product exposed to oil? Samples and technical help are yours by writing to:

Goodyear, Chemical Division,
Rubber & Rubber Chemicals Dept.,
Akron 16, Ohio

CHEMICAL GOODYEAR DIVISION

Chemigum, Pliobond, Pliolite, Plio-Tuf, Pliovic—T. M.'s The Goodyear Tire & Rubber Company, Akron, Ohio

The Finest Chemicals for Industry—CHEMIGUM • PLIOBOND • PLIOFLEX • PLIOLITE • PLIO-TUF • PLIOVIC • WING-CHEMICALS

Announcing VA-7

... an economical vulcanizing agent for heat-resistant, non-blooming stocks

VA-7 is a new liquid vulcanizing agent for all types of unsaturated elastomers. It provides economical "sulfurless" cures for nitrile, GR-S and natural rubber stocks.

Stocks compounded with VA-7 display an outstanding combination of heat aging resistance . . . . high tensile strengths . . . . good hot compression set resistance . . . . and non-blooming characteristics in the cured and uncured states.

VA-7 also offers processing advantages—it can be dispersed more easily and uniformly than sulfur. Stable emulsions for curing latices can easily be prepared from VA-7.

The moderate price of VA-7 is another feature that makes this product worth your investigation. *Try VA-7 for heat-resistant, non-blooming stocks at reasonable cost!*

For compounding information and a sample of VA-7 fill out and mail the handy coupon.

CHECK LIST OF VA-7 PROPERTIES

Outstanding heat aging resistance
Non-blooming in cured or uncured state
High strengths at low concentrations
Easy and uniform dispersion
Good hot compression set
Moderate price

THIOKOL CHEMICAL CORPORATION
780 N. Clinton Avenue
Trenton 7, New Jersey

Please send me compounding information ☐
and a sample of VA-7 ☐

NAME _____ FUNCTION _____
COMPANY _____
STREET _____
CITY AND ZONE _____ STATE _____

Thiokol Chemical Corporation
780 NORTH CLINTON AVENUE • TRENTON 7, NEW JERSEY

Your Product Deserves

DU PONT RUBBER CHEMICALS

DEPENDABLE IN PERFORMANCE...UNIFORM IN QUALITY

ACCELERATORS

Accelerator 89
Accelerator 552
Accelerator 808
Accelerator 833
Butyl Accelerator 21
DOTG
MBT
MBTS
NA-22
Permalux
Polyac
Tepidone
Tetrone A
Thionex
Thionex Grains
Thiuram E
Thiuram M
Thiuram M Grains
Zenite
Zenite A
Zenite Special

ANTIOXIDANTS

Akroflex C
Akroflex CD
Antox
Neozone A
Neozone D
Permalux
Thermoflex A

AQUAREXES

Aquarex L
Aquarex D
Aquarex G
Aquarex MDL
Aquarex ME
Aquarex NS
Aquarex SMO
Aquarex WAQ

BLOWING AGENTS

Unicel ND
Unicel S

COLORS

RUBBER DISPERSED COLORS	RUBBER DISPERSED COLORS
Rubber Red PBD	Rubber Green GSD
Rubber Red ZBD	Rubber Blue PCD
Rubber Yellow GD	Rubber Blue GD
Rubber Green FD	Rubber Orange OD

ORGANIC ISOCYANATES

Hylene*M
Hylene*M-50

PEPTIZING AGENTS

RPA No. 2
RPA No. 3
RPA No. 3 Concentrated
RPA No. 5
RPA No. 6

RECLAIMING CHEMICALS

RPA No. 3
RR-10

SPECIAL-PURPOSE CHEMICALS

Barak—Accelerator activator
Copper Inhibitor X-872-L—Inhibits catalytic action of copper on elastomers
ELA—Elastomer lubricating agent
Hellozone—Sun-checking inhibitor
NBC—Inhibits weather cracking of GR-S
Retarder W—Accelerator retarder

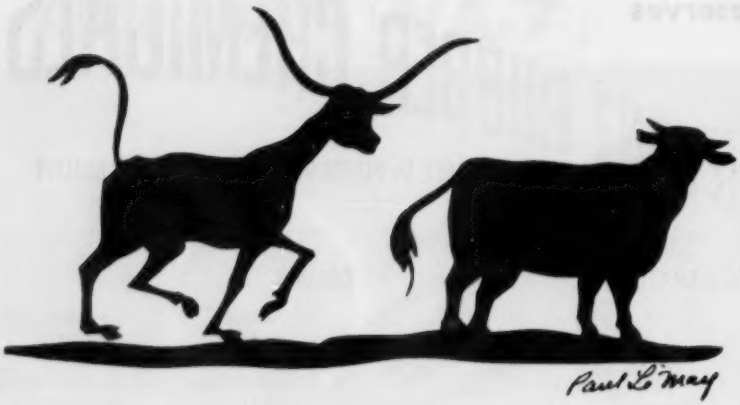
E. I. du Pont de Nemours & Co. (Inc.)
Elastomers Division

*TRADE-MARK

DU PONT
BETTER THINGS FOR BETTER LIVING ...THROUGH CHEMISTRY

DISTRICT OFFICES:

Akron 8, Ohio, 40 East Buchtel Ave. at High Street . POrtage 2-8461
Atlanta, Ga., 1261 Spring St., N. W. . . . . EMerson 5391
Boston 10, Mass., 140 Federal St. . . . . HAncock 6-1711
Charlotte 2, N. C., 427 West Fourth St. . . . . CHarlotte 5-5561
Chicago 3, Ill., 7 South Dearborn St. . . . . ANdover 3-7000
Detroit 35, Mich., 13000 West 7-Mile Rd. . . . . UNiversity 4-1963
Houston 25, Texas, 1100 E. Holcombe Blvd. . . . . JAckson 8-1432
Los Angeles 58, Calif., 2930 E. 44th St. . . . . LOgan 5-6464
Trenton 8, N. J., 1750 North Olden Ave. . . . . EXport 3-7141
In Canada contact Du Pont Company of Canada Limited, Box 660, Montreal.



...changed

The beef steer of today is a big change from the longhorn of yesteryear. Compounding practices have changed, yet the demand for large quantities of ***TEXAS CHANNEL BLACKS*** remains unchanged.

TEXAS CHANNEL BLACKS offer many savings when used alone or in combination with other types of carbon blacks. Numerous tests and actual performance indicate that with the use of ***TEXAS CHANNEL BLACKS*** savings can be obtained with no loss in ultimate performance.

TEXAS CHANNEL BLACKS

Sid Richardson CARBON CO.

FORT WORTH, TEXAS

GENERAL SALES OFFICES EVANS SAVINGS AND LOAN BUILDING AKRON 8, OHIO

How long did it take . . .
to get from here . . . to here?

Answer: 25 years

With the introduction of hot water heaters in 1926 cars, motorists were beginning to roll in solid comfort during cold winter months. But research and development didn't stop there. Since 1951, air conditioning, at the touch of a button, provides year-'round spring temperatures despite weather extremes.

At the same time, the rubber industry was discovering new ways of making its products more versatile and longer lasting. Monsanto has played an important role in this development with its increasing number of rubber chemical products.

For example, Santocure NS, the newest Monsanto accelerator of the sulfenamide type, is characterized by even more delayed action, greater strength and full activity at curing temperatures. As an analogue of regular Santocure it is designed to meet the needs of present day high-speed production which involves high processing temperatures.

For your copy of catalog "Chemicals for the Rubber Industry," write MONSANTO CHEMICAL COMPANY, Rubber Chemicals Dept., 920 Brown St., Akron 11, Ohio.

MONSANTO CHEMICALS FOR THE RUBBER INDUSTRY

ANTIOXIDANTS
Flectol* H
Santoflex* DD
Santoflex 75
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L
Santowhite Powder

ALDEHYDE AMINE ACCELERATORS
A-32*
A-100*

MERCAPTO ACCELERATORS
Saniocure* NS
Santocure
El-Sixty*
Mertax* (Purified Thiotax)
Thiotax* (2-Mercaptobenzothiazole)
Thiofide* [2,2'-dithiobis (benzothiazole)]
Thiofide S (Seed Form)

GUANIDINE ACCELERATORS
Diphenylguanidine (D.P.G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.
R-2 Crystals*
RZ-50-A*
RZ-50-B*
Thiurad* (Tetramethylthiuram-disulfide)
Mono Thiurad* (Tetramethylthiuram-monosulfide)
Ethyl Thiurad* (Tetraethylthiuram-disulfide)

MONSANTO
CHEMICALS – PLASTICS

WHERE CREATIVE CHEMISTRY WORKS WONDERS FOR YOU

SPECIAL MATERIALS
Thiocarbanilide ("A-1")
Santovar*-A
Sulfasan* R
Insoluble Sulfur "60"
COLORS
REODORANTS

*Reg. U. S. Pat. Off.

Diary of an old shoe

"Walked, walked, walked—on pavement and dirt—month after month—mile after mile, rain or shine . . ."

But this shoe could take it! It is one of millions of shoes that have the modern type of rubber sole reinforced by the incorporation of high styrene resins and plasticized with low cost **PANAREZ** hydrocarbon resins.

PANAREZ resins are tack producing agents and rubber softeners which make definite improvements in "flex crack", abrasion and tear resistance, tensile strength, and aging properties. At the same time, **PANAREZ** resins permit the use of larger than normal quantities of filler without sacrificing quality. This has resulted in important reductions in raw material costs.

PANAREZ resins, derived from petroleum, act excellently as polymeric plasticizers. They provide excellent color and color stability. They have low specific gravity. They are particularly useful in GRS rubbers where improvements in processability and stock physicals are desired—at a simultaneously reduced cost.

Whether you compound or use rubber for shoe soles, wire covering, floor tiles, tires, hose, insulators or some other products, we welcome the opportunity to work confidentially with you on your particular problem. Readily available in various color grades and unlimited quantities, **PANAREZ** resins offer the compounder a completely reliable, low cost raw material.

For full information write or wire Dept. RC.

AN AMOCO PRODUCT

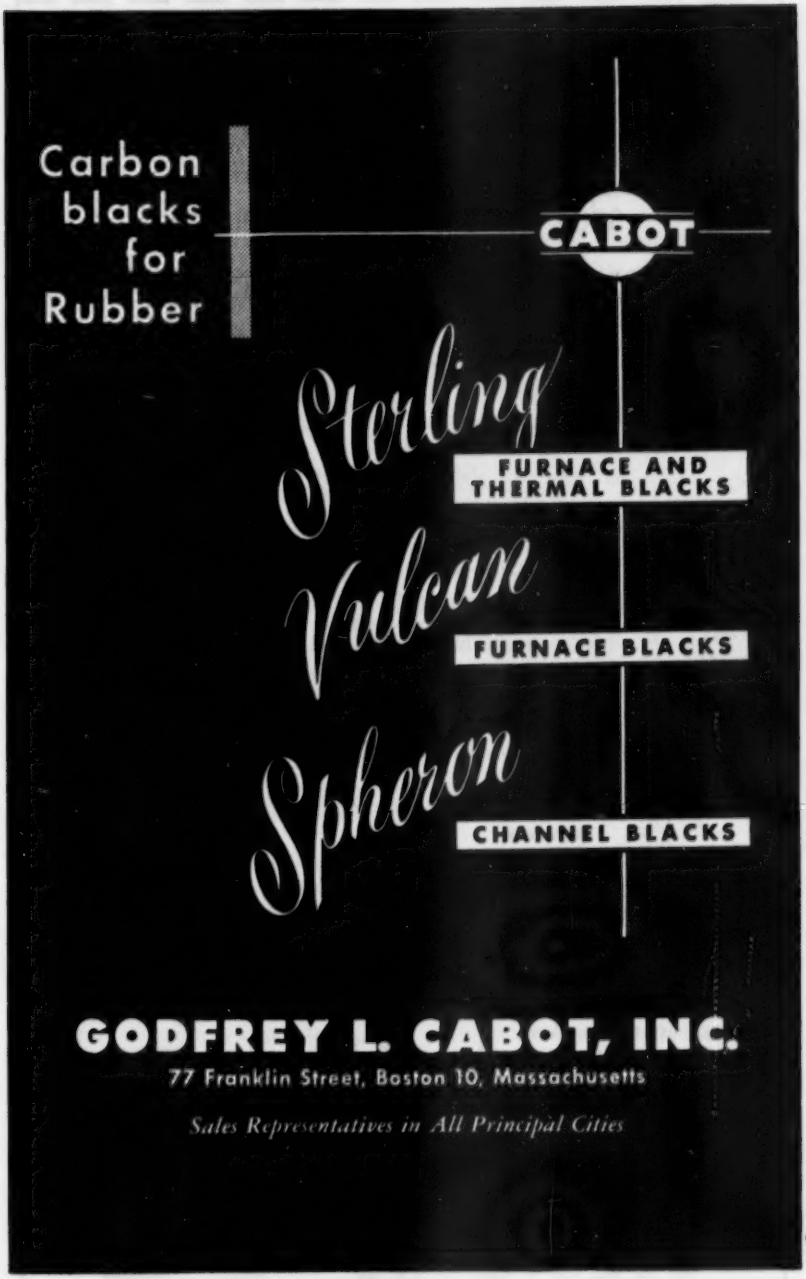
PAN AMERICAN CHEMICALS CORP

555 FIFTH AVENUE, NEW YORK 17, N. Y.

HYDROCARBON PANAREZ RESINS

PANAPOL
Hydrocarbon drying oils

PANASOL
Aromatic solvents


Carbon blacks for Rubber
CABOT
Sterling
FURNACE AND THERMAL BLACKS
Vulcan
FURNACE BLACKS
Spheron
CHANNEL BLACKS
GODFREY L. CABOT, INC.
77 Franklin Street, Boston 10, Massachusetts
Sales Representatives in All Principal Cities

A Leader in Rubber Chemicals Research

Cyanamid

adds two recent developments

NOBS* SPECIAL Accelerator and ANTIOXIDANT 425*

to its top-quality line...

ACCELERATORS

Thiazoles

MBT (Mercaptobenzothiazole)
MBT-XXX (Specially Refined—Odorless)
MBTS (Benzothiazyldisulfide)
NOBS* No. 1 Accelerator
NOBS* SPECIAL Accelerator

Guanidines

DPG (Diphenylguanidine)
DOTG (Diorthotolylguanidine)
Accelerator 49

ANTIOXIDANTS

Antioxidant 2246®
Antioxidant 425*

PEPTIZER

Pepton® 22 Plasticizer

RETARDER

Retarder PD

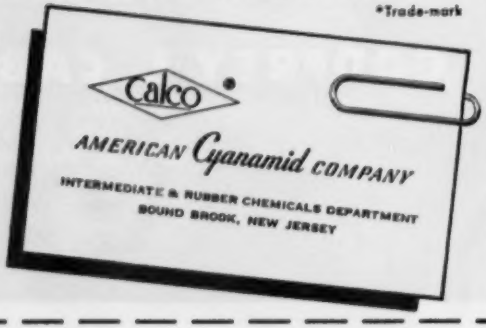
SULFUR

Rubber Makers' Grades

—with further significant research achievements still to come!

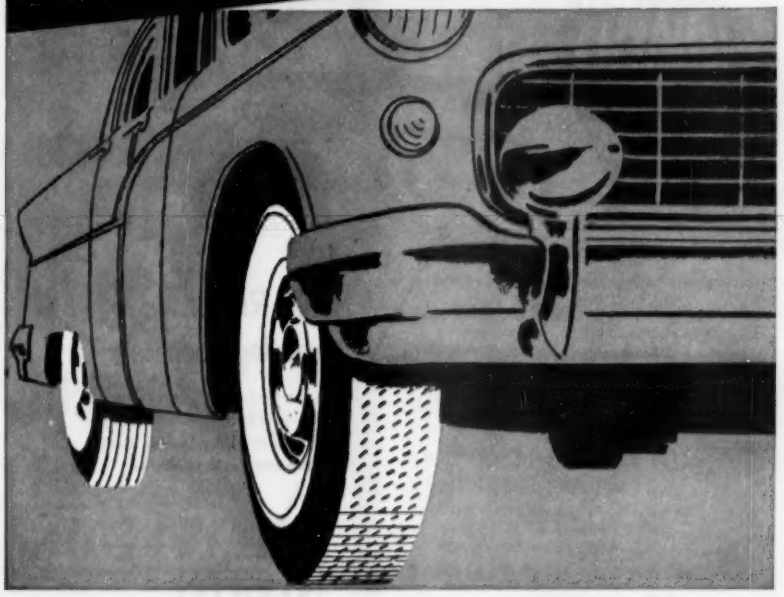
*Trade-mark

SALES REPRESENTATIVES AND WAREHOUSE STOCKS: Akron Chemical Company, Akron, Ohio • H. M. Royal, Inc., Trenton, N. J. • H. M. Royal, Inc., Los Angeles, Calif. • Ernest Jacoby and Company, Boston, Mass. • Herron & Meyer of Chicago, Chicago, Ill. • In Canada: St. Lawrence Chemical Company, Ltd., Montreal and Toronto.



1956 Model...

Equipped with STYRENE MONOMER



Styrene Monomer is an indispensable ingredient of GR-S synthetic rubber, widely used in the manufacture of tough, puncture-resistant tubeless tires. Because GR-S rubber tires possess *toughness with flexibility*, they wear longer and are better able to withstand punishment.

Styrene Monomer is used in the manufacture of other styrene-butadiene copolymers for commercial rubber applications. These include shoe soles and heels, hose, floor tile, luggage, apparel accessories, industrial conveyor belts and power transmission belting, gaskets, grommets, wire coating, and a wide variety of others.

Look to Koppers for a dependable source of supply for Styrene Monomer. You'll have it where you need it, when you need it. For further information, write to: KOPPERS COMPANY, INC., Chemical Division, Dept. RCT-125, Pittsburgh 19, Pennsylvania.

SALES OFFICES: New York • Boston • Philadelphia • Atlanta • Houston • Chicago • Detroit • Los Angeles

KOPPERS

KOPPERS CHEMICALS

Keep Your Quality Sky-High!

with
Neville Rubber Processing Chemicals

Their standard specifications insure consistently uniform compounds of high quality. In addition, they provide down-to-earth economies in production.

NEVILLE

COUMARONE-INDENE RESINS
PETROLEUM RESINS
RUBBER RECLAIMING OILS

NEVILLE CHEMICAL CO. PITTSBURGH 25, PA.

Plants at Neville Island, Pa., and Anaheim, Cal.

RSS

For Accelerators, Activators, Anti-Oxidants and Special Rubber Chemicals

TRY NAUGATUCK

NAUGATUCK supplies a complete line of proven accelerators, activators, anti-oxidants, and special chemicals to give you thorough control of rubber product manufacture and performance.

ACCELERATORS

THIAZOLES—
M-B-T
M-B-T-S O-X-A-F

THIURAMS—
MONEX*† TUEX†
MORFEX ETHYL TUEX†
PENTEX*

DITHIOCARBAMATES—
ARAZATE* ETHAZATE*†
BUTAZATE* METHAZATE*†
ETHAZATE-50D

ALDEHYDE AMINES—
BEUTENE* HEPTEEN BASE*
TRIMENE* TRIMENE BASE*

XANTHATES—
C-P-B* Z-B-X*

ACTIVATORS

VULKLOR DIBENZO G-M-F
D-B-A G-M-F

ANTI-OXIDANTS

AMINOX* B-L-E*
ARANOX* B-X-A
V-G-B* FLEXAMINE
OCTAMINE* BETANOX* Special

SPECIAL PRODUCTS

BWH-1 SUNPROOF* Improved
CELOGEN SUNPROOF* Junior
CELOGEN-AZ SUNPROOF*—713
E-S-E-N SUNPROOF* Regular
LAUREX* SUNPROOF* Super
TONOX* KRALAC* A-EP

SPECIAL PRODUCTS FOR SYNTHETIC POLYMERS

DDM—modifier
THIOSTOP K&N—short stops
POLYGARD—stabilizer

*Reg. U. S. Pat. Off.

THE WORLD'S LEADING MANUFACTURER OF RUBBER CHEMICALS

LOOKING FOR...
Plastics
Reclaimed Rubber
Synthetic Rubber
Latices

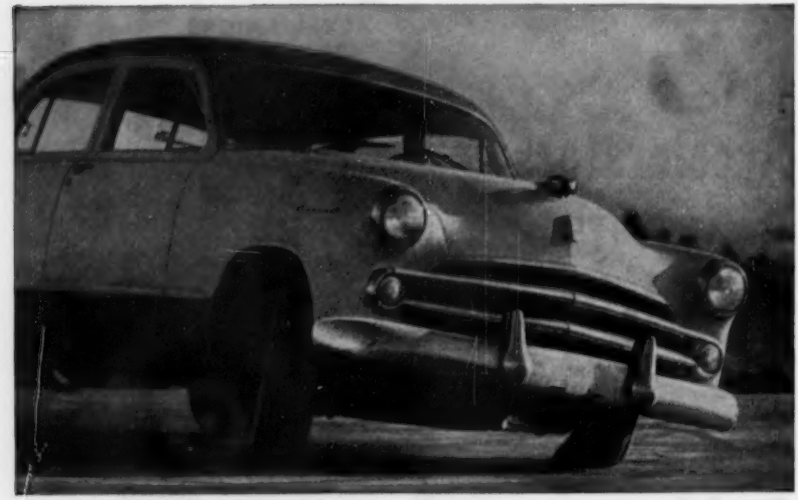
Write, on your letterhead, for technical data or assistance with any Naugatuck product.

†these products furnished either in powder form or fast-dispersing, free-flowing NAUGETS.

Naugatuck Chemical

Division of United States Rubber Company
Naugatuck, Connecticut

BRANCHES: Akron • Boston • Charlotte • Chicago • Los Angeles • Memphis • New York • Philadelphia
IN CANADA: Naugatuck Chemicals, Elmira, Ontario • Rubber Chemicals • Synthetic Rubber • Plastics • Agricultural Chemicals • Reclaimed Rubber • Latices • Cable Address: Rubexport, N.Y.



FOR TOUGHER, LONGER MILEAGE TUBELESS TIRES THAT DON'T SQUEAL...USE CIRCOSOL-2XH

Taking the objectionable squeal out of the new tubeless tires—without sacrificing abrasion resistance or toughness—is a problem in tread compounding as well as tread design. Tread design, of course, is somebody else's problem. But Sun's Circosol-2XH will solve your compounding problem.

The unique properties of Sun's Circosol-2XH are due to its scientifically controlled balance of naphthenic and aromatic hydrocarbons. By using Circosol-2XH in your tread stock, you can get a tubeless tire with high abrasion resistance, high flex-crack resistance, long mileage...and most important, it will be quiet running.

The cost of these extra advantages of Circosol-2XH is low. Enough Circosol-2XH for an 8.00 x 15 size, 100 level tire costs less than 2¢ more than the cheapest softener you can possibly buy.

Get the full story on both the advantages *and the new low price* of Circosol-2XH from your Sun representative...or write at once to SUN OIL COMPANY, Philadelphia 3, Pa., Dept. RC-10.

SUNOCO

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY Philadelphia 3, Pa.

IN CANADA: SUN OIL COMPANY, LTD., TORONTO AND MONTREAL

OCTOBER-DECEMBER • 1955

VOLUME XXVIII • NUMBER FOUR

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

CARBON BLACKS

for RUBBER COMPOUNDING

ISAF (Intermediate Super Abrasion Furnace)
STATEX®-125

HAF (High Abrasion Furnace)
STATEX-R

MPC (Medium Processing Channel)
STANDARD MICRONEX®

EPC (Easy Processing Channel)
MICRONEX W-6

FF (Fine Furnace)
STATEX-B

FEF (Fast Extruding Furnace)
STATEX-M

HMF (High Modulus Furnace)
STATEX-93

SRF (Semi-Reinforcing Furnace)
FURNEX®

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON COMPANY

380 Madison Ave. New York 17, N.Y.

RUBBER CHEMISTRY AND TECHNOLOGY

Published Quarterly under the Auspices of the Division of Rubber Chemistry
of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. DAVIS
Advertising Manager ..... E. H. KRISMANN
Secretary ..... A. M. NEAL
Treasurer ..... G. E. POPP

Vol. XXVIII October-December, 1955 No. 4

CONTENTS

General Section

PAGE

Officers iii
Fall Meeting of the Division of Rubber Chemistry, New York, N. Y., September 15–17, 1954 vi
Spring Meeting of the Division of Rubber Chemistry, Detroit, Michigan, May 4–6, 1955 viii
New Books and Other Publications xi

Papers

Carboxylic Elastomers. HAROLD P. BROWN AND CARLIN F. GIBBS 937
Butyl-Type Polymers Containing Bromine. R. T. MORRISSEY 952
Study of the Reaction Kinetics of Aging of Natural Rubber by Means of Infrared Spectrography. III. Effect of Light and Influence of Antioxidants. V. KELLÖ AND T. TKÁČ 968
Study of the Reaction Kinetics of Aging of Natural Rubber by Infrared Spectrography IV. Influence of Wave Length of Light and Temperature on Light Aging. A. TKÁČ, V. KELLÖ, AND J. HRIVÍKOVÁ 989
X-Ray Determination of Crystallinity in Deformed Rubber. S. C. NYBURG 999
Nature of Stark Rubber. DONALD E. ROBERTS AND LEO MANDELKERN 1007
Bisalkylation Theory of Neoprene Vulcanization. PETER KOVACIC 1021
Combination of Rubber and Carbon Black on Cold Milling. W. F. WATSON 1032
Determination of the Fatigue Resistance of Rubber Parts under Cyclic Shear Stress in Relation to Their Shape and Energy. HERMANN ROELIG AND GUIDO FROMANDI 1044
New Instruments for Measuring Hardness. STEFANO OBERTO 1054
Rubber Hardness Testing. J. R. SCOTT 1071
Abrasion and Slippage. G. EBERT AND V. WEIDNER 1082
Ozone Resistance of Butyl Vulcanizates. D. C. EDWARDS AND E. B. STOREY 1096
Ozone Crazing of Biaxially Stressed GR-S Vulcanizates. Z. T. OSSEFORT AND W. J. TOUHEY 1119
Softening of Vulcanized Carbon Black-Loaded Rubber During Extension. D. G. MARSHALL, D. L. WALKER, AND J. G. SMITH 1123

Correlation of Room-Temperature Shelf Aging with Accelerated Aging. R. A. Youmans and G. C. Maassen 1133
The Shrinkage of Mold Cured Elastomer Compositions. A. E. Juve and J. R. Beatty 1141
Temperature Control During Mixing of Rubber Compounds. Frank L. Roth, George E. Decker, and Robert D. Stiehler 1157
A Study of Some Heat-Sensitizing Agents for Hevea Latex. Claude Pariente ... 1166
Influence of Salt Coagulants on the Properties and on the Aging of Rubber Products Made by the Dipping Process. A. Thorsrud 1175
Effect of Sulfuric Acid Coagulation on Properties of Natural Rubber. L. L. Best and S. H. Morrell 1185
The Accelerated Coagulation of Latex. G. E. Van Gils and W. L. Resing 1193
The Significance of the Yellow Fraction in Spontaneous Coagulation. F. J. Paton 1204
Zinc Oxide Testing of Latex. E. W. Madge, H. M. Collier, and J. L. M. Newham 1211
Determination of Free Sulfur in Hard Rubber. C. Wynne-Evans 1221
Promotors for the Reaction of Rubber with Carbon Black. Kenneth W. Doak, George H. Ganzhorn, and Bernard C. Barton 1226
Author Index 1228
Subject Index 1230

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($4.00 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of $6.50 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at the subscription price of $7.50 per year.

To these charges of $4.00 and $7.50, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications to become Members or Associates of the Division of Rubber Chemistry, with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, George E. Popp, Phillips Chemical Co., 318 Water St., Akron 8, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman.....A. E. JUVE, B. F. Goodrich Research Center, Brecksville, O.
Vice-Chairman.....B. S. GARVEY, Sharples Chemicals, Inc., Wayne, Pa.
Secretary...A. M. NEAL, E. I. du Pont de Nemours & Co., Wilmington, Del.
Treasurer.....G. E. POPP, Phillips Chemical Co. 318 Water St., Akron 8, O.
Editor of *Rubber Chemistry and Technology*....C. C. DAVIS, Boston Woven Hose and Rubber Co., Cambridge, Mass.
Advertising Manager of *Rubber Chemistry and Technology*....E. H. KRISMANN, E. I. du Pont de Nemours & Co., Akron, O.
Directors....J. M. BALL (Past Chairman), D. C. MADDY (Director-at-Large), L. M. BAKER (Akron), W. S. EDSALL (Boston), H. E. ELDEN (Buffalo), B. W. HUBBARD (Chicago), C. A. LARSON (Connecticut), H. W. HOERAUF (Detroit), D. F. REAHARD (Fort Wayne), B. R. SNYDER (Los Angeles), J. A. BRECKLEY (New York), J. M. HOLLOWAY (Northern California), G. J. WYROUGH (Philadelphia), U. J. H. MALO, (Rhode Island), E. N. CUNNINGHAM (Southern California), R. D. STIEHLER (Washington, D. C.)
Councillors....A. M. NEAL, 1955–1958;
(Alternates, C. S. YORAN, 1955–1958;).

OFFICERS OF LOCAL RUBBER GROUPS

AKRON

Chairman..K. R. GARVICK (Mansfield Tire and Rubber Co., Mansfield, Ohio). *Vice-Chairman*....H. M. BRUBAKER (Witco Chemical Co., Akron). *Secretary*....GEORGE HACKIM (General Tire and Rubber Co., Akron). *Treasurer*..H. W. CATT (The B. F. Goodrich Co., Akron). Terms end June 30, 1956. Meetings will be October 28, 1955 and January 27, April 6, and June 15 (Summer Outing) 1956.

BOSTON

Chairman....E. D. COVELL (Stedfast Rubber Co., Mattapan, Boston). *Vice-Chairman*....J. E. WILLIAMSON (Tyer Rubber Co., Andover). *Secretary-Treasurer*....A. I. ROSS (American Biltrite Rubber Co., Chelsea). Terms end December 31, 1955. Meetings in 1955, March 25, June 17, October 14, and December 16.

BUFFALO

Chairman....C. E. JOHNSON (Hewitt-Robins, Inc., Buffalo). *Vice-Chairman*....P. J. SCHWERT (Dunlop Rubber Co., Buffalo). *Secretary-Treasurer*....C. W. WAHL (Hewitt-Robins, Inc.). Terms end December 31, 1955. Meetings in 1955, March 8, May 20, June 16, October 4, and December 7.

CHICAGO

Chairman....L. W. HEIDE (Acadia Synthetic Products Division, Western Felt Works, Chicago). *Vice-Chairman*....A. E. LAURENCE (Phillips Chemical

Co., Addison, Ill). *Secretary*....V. J. La Brecque (Victor Mfg. and Gasket Co., Chicago). *Treasurer*....M. J. O'Connor (O'Connor and Co., 333 N. Michigan Ave., Chicago). Terms end August 30, 1955. Meeting dates are October 7, November 11, December 16, 1955 and February 17, March 16, April 27, 1956.

Connecticut

Chairman....W. E. Fisher (Armstrong Rubber Co., West Haven). *Vice-Chairman*....J. R. Boyle (Armstrong Rubber Co., West Haven). *Secretary*....N. W. Hess (United States Rubber Co., Naugatuck). *Treasurer*.... Harry Gordon (Bond Rubber Co., Derby). Terms end December 31, 1955. Meetings in 1955, February 18, May 20, September 17, and November 18.

Detroit

Chairman....J. T. O'Reilly (Ford Motor Co., Detroit). *Vice-Chairman*....H. W. Hoerauf (United States Rubber Co., Detroit). *Treasurer*.... W. F. Bauer (Brown Rubber Co., Inc., Detroit). *Secretary*....H. F. Jacober (Baldwin Rubber Co., Pontiac). Terms end December 31, 1955. Meetings in 1955, February 4, June 24, October 7, December 9.

Fort Wayne

Chairman....Jack Carlson (Paranite Wire and Cable Co., Marion, Indiana). *Vice-Chairman*....M. J. O'Connor (O'Connor and Co., 333 N. Michigan Ave., Chicago, Ill.). *Secretary-Treasurer*....John Dixon (Anaconda Wire and Cable Co., Marion, Indiana). Terms end August 31, 1956. Meeting dates are September 29, December 1, 1955, February 9 and April 12. 1956.

Los Angeles

Chairman....F. C. Johnston (Caram Manufacturing Co., Monrovia). *Associate Chairman*....C. S. Hoglund (R. D. Abbott Co., Inc., Los Angeles). *Vice-Chairman*....Atlas Sponge Rubber Co., Los Angeles). *Secretary*.... C. H. Kuhn (Master Processing Corp., Lynwood). *Treasurer*....A. H. Federico (C. P. Hall Company of California, Los Angeles). Terms end December 31, 1955. Meetings in 1955, February 1, March 1, April 6, May 3, June 4–5, October 4, November 1, and December 9.

New York

Chairman....S. M. Martin, Jr. (Thiokol Chemical Corp., Trenton, J. N.). *Vice-Chairman*....G. H. Provost (United States Rubber Co., Passaic, N. J.). *Sergeant-at-Arms*....T. A. Bulifant (Barrett Division, Allied Chemical and Dye Corp., Edgewater, N. J.). Terms end December 1955. Meetings in 1955, April 1, June 9, October 7, December 9.

Northern California

Chairman....H. C. Burke (Burke Rubber Co., San Jose). *Vice-Chairman*....Leonard Evans (Mansfield Tire and Rubber Co., Oakland). *Secretary*....Eugene Gador (Oliver Tire and Rubber Co., Emeryville). Terms end December 31, 1955. Meetings in 1955, April 14, May 12, June 9, October 13, November 10. Picnic in September and Christmas party in December.

PHILADELPHIA

Chairman....M. A. YONKER (E. I. du Pont de Nemours & Co., Wilmington Del.). *Vice-Chairman*....L. E. WHITE (Walker Bros., Conshohocken, Penn.). *Secretary-Treasurer*....R. J. SALYERDS (Harwick Standard Chemical Co., Trenton, N. J.). Terms end January 15, 1956. Meetings in 1955, April 29, August 19, and November 18.

RHODE ISLAND

Chairman....U. J. H. MALO (Crescent Co., Inc., Pawtucket). *Vice-Chairman*....R. W. SZULIK (Acushnet Process Co., New Bedford, Mass.). *Secretary-Treasurer*....G. E. ENSER (Collyer Wire Co., Pawtucket). Terms end November 1955. Meetings in 1955, March 31, June 2, November 3.

SOUTHERN OHIO

Chairman....FRANK NEWTON (Dayton Rubber Co., Dayton). *Vice-Chairman*....J. R. WALL (Inland Manufacturing Division, General Motors Corp., Dayton). *Secretary*....R. J. HOSKIN (Inland Manufacturing Division, General Motors Corp., Dayton). *Treasurer*....R. C. HEMPELMAN (Preimer Rubber Manufacturing Co., Dayton). Terms end December 31, 1955. Meetings in 1955, March 31, June 4, September 22, December 10.

WASHINGTON D. C.

Chairman....P. S. GREER (Office of Synthetic Rubber, Reconstruction Finance Corporation, Washington). *Vice-Chairman*....W. J. SEARS (Rubber Manufacturers' Association, Washington). *Secretary*....W. B. DUNKLE (Goodyear Tire & Rubber Co., Washington). *Treasurer*....(MISS) ETHEL LEVENE (Las Cruces, New Mexoci). *Recording Secretary*....(MISS) R. J. FANNING (National Bureau of Standards). Terms end October 1955. Meetings in 1955, February 16, March 16, April 20, May 18, June outing, October, Christmas Party.

FUTURE MEETINGS

The Division of Rubber Chemistry of the American Chemical Society is scheduled to hold meetings in the following cities in 1955, 1956, and 1957.

Meeting	*City*	*Hotel*	*Date*
1956 Spring	Cleveland*	Cleveland	May 16–18
1956 Fall	Atlantic City	—	September 19–21
1957 Spring	Montreal*	Sheraton-Mt. Royal	May 15–17
1957 Fall	New York	—	September 11–13

* The meeting will be held independent of, and at a different time from, the corresponding spring or fall meeting of the American Chemical Society.

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY, NEW YORK, N. Y., SEPTEMBER 15–17, 1954

The 66th Meeting of the Division of Rubber Chemistry was held in New York, September 15–17, 1954, with headquarters at the Hotel Commodore. The best estimate of attendance was that 1200 people were attracted to the

American Chemical Society meeting by the activities of the Rubber Division.

The 25-Year Club met under the Chairmanship of B. R. Silver, with approximately 250 people present. The contest for the longest service in the rubber industry was won by Frank Baker (Landers Corp.).

At the banquet, over 600 people were present. The highlights of the banquet were the presentation of the Goodyear Medal and scroll to G. Stafford Whitby of the University of Akron, and the recognition of S. G. Byam on his completion of twenty-one consecutive years of service on the Executive Committee of the Division.

At the Executive Committee meeting a new committee was established. This committee is designated as the Educational Committee, and will advise the officers of the Rubber Division regarding the proper activities of the Division in the field of education and will serve as a clearing house to coordinate the increasing activities of the various rubber groups in providing educational courses in the field of rubber technology.

The Executive Committee elected L. S. Cooper, S. B. Kuykendall, and E. H. Krismann as members of the newly created Finance Committee. Acting on advice of the Finance Committeee, the Division has created a safekeeping fund in the First National Bank at Akron.

It was reported that maintenance of the Library through March 1955 has been assured, and action was taken which is expected will maintain its activities for at least a five-year period.

At the business meeting recognition was made of the deaths since the last meeting of H. M. Frecker and H. G. Eckhardt.

The following papers were presented:

Studies on the Determination of Relative Road-Wear Ratings of Tire-Tread Stocks. E. M. Dannenberg and F. H. Amon (Godfrey L. Cabot, Inc., Boston, Mass.).

Relaxed Compression Set—A Definitive Property of Vulcanizates. L. R. Sperberg (Sid Richardson Carbon Co., Odessa, Tex.).

Fatigue of Rubber with Two-Way Stretching. S. D. Gehman and R. P. Clifford (Goodyear Tire and Rubber Co., Akron, O.).

Smearing of Vulcanized Rubber. C. S. Wilkinson, Jr., S. D. Gehman, and R. D. Daniels (Goodyear Tire and Rubber Co., Akron, O.).

Milling Procedure: Its Effect on Physical Properties. B. J. A. Martin and D. Parkinson (Research Centre, Dunlop Rubber Co., Ltd., Birmingham, England).

Correlation of Room-Temperature Shelf Aging with Accelerated Aging. G. C. Maassen (R. T. Vanderbilt Co., New York, N. Y.) and R. A. Youmans (Kirkhill Rubber Co.).

The History of the Rubber Latex Industry. E. A. Hauser (Massachusetts Institute of Technology, Cambridge, Mass.).

KEL-F Elastomer: A New Fluorocarbon Rubber. M. E. Conroy, L. E. Robb, D. R. Wolf and F. J. Honn (M. W. Kellogg Co., Jersey City, N. J.).

Compounding Studies of Copolymers of Chlorotrifluoroethylene. J. C. Montermoso and C. B. Griffis (Quartermaster Research and Development Center, U. S. Army, Natick, Mass.).

KEL-F Elastomer—Fabrication and Applications. L. E. Robb, D. R. Wolf, M. E. Conroy and F. J. Honn (M. W. Kellogg Co., Jersey City, N. J.).

Fluorocarbon Rubber Research. F. J. Honn, J. M. Hoyt, A. N. Bolstad, (M. W. Kellogg Co., Jersey City, N. J.) and C. B. Griffis and J. C.

Montermoso (Quartermaster Research and Development Center, U. S. Army, Natick, Mass.).
Poly-FBA: A Fluorine-Containing Polyacrylic Rubber. P. J. Stedry and J. F. Abere (Minnesota Mining & Manufacturing Co., St. Paul, Minn.).
Reflections on Rubber Research—The Goodyear Lecture. G. Stafford Whitby (University of Akron, Akron, O.).
Carboxylic Elastomers. H. P. Brown and C. F. Gibbs (B. F. Goodrich Research Center, Brecksville, O.).
Butyl-Type Polymers Containing Bromine. R. T. Morrissey (B. F. Goodrich Research Center, Brecksville, O.).
Sulfur-Curable Silicone Rubber Compositions and Blends with Hydrocarbon Elastomers. D. T. Hurd and R. C. Osthoff (General Electric Research Laboratory, Schenectady, N. Y.).
Morphological Studies of Elastic Silicones. E. A. Hauser (Massachusetts Institute of Technology, Cambridge, Mass.).
Fibrous Rubber, Its Production and Properties. Worth Wade, L. R. B. Hervey, D. E. Till, and R. M. Winters, Jr. (American Viscose Corp., Philadelphia, Pa.).
Amine Activators for Emulsion Copolymerization of Butadiene and Acrylonitrile. H. L. Williams and J. W. L. Fordham (Polymer Corp., Ltd., Sarnia, Ontario).
Butadiene/Styrene Copolymers—100% Conversion of Monomers. T. W. Boyer and N. R. Legge (Kentucky Synthetic Rubber Corp., Louisville, Ky.).
The Analytical Determination of Some Elastomeric Components in Aqueous Extracts. K. Marcali (Jackson Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Del.).
Identification of Curing Agents in Rubber Products—Ultraviolet Adsorptiometric Analysis of Selective Solvent Extracts. F. G. Stevens and K. E. Kress (The Firestone Tire and Rubber Co., Akron, O.).
The Identification of Accelerators and Antioxidants in Vulcanized Rubber Products. G. D. Louth and M. J. Brock (The Firestone Tire and Rubber Company, Akron, O.).
The Stoichiometry and Fate of Oxidation Inhibitors in Benzene and Chlorobenzene. G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen (Chemical Laboratory, Iowa State College, Ames, Iowa).
Determination of Latex Particle Size by Absorption of Electrolytes. S. R. Ogilby (The Goodyear Tire & Rubber Co., Akron, O.).
Dry Compounding vs. Latex Masterbatching of Oil Extended GR-S. F. S. Rostler and R. M. White (Golden Bear Oil Co., Oildale, Cal.).
Alkyl Amates as Elastomer Plasticizers. A. W. Campbell (Commercial Solvents Corp., Terre Haute, Ind.).
A Bis-Alkylation Theory of Neoprene Vulcanization. Peter Kavocic (Jackson Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Del.).
Inhibition of Rubber Oxidation by Carbon Black. K. A. Burgess and C. W. Sweitzer (Columbian Carbon Co., New York, N. Y.).
Rubber-Filler Interactions—Solution Adsorption Studies. E. B. Gutoff and E. R. Gilliland (Massachusetts Institute of Technology, Cambridge, Mass.).
The Surface Treatment of Hydrated Silica Pigments for the Reinforcement of Rubber Stocks. R. S. Stearns and B. L. Johnson (The Firestone Tire & Rubber Co., Akron, O.).

The Geometric Construction of Copolymer Solvent Phase Diagrams. F. W. Boggs (General Laboratories, U. S. Rubber Co., Passaic, N. J.).

Polymer Networks Formed in the Presence of Diluent. A. J. Costanza, R. M. Pierson and F. J. Naples (The Goodyear Tire & Rubber Co., Akron, O.).

Recent Developments in Rubber-to-Metal Bonding. H. H. Irvin and W. H. Cornell (Marbon Corp., Division of Borg-Wagner, Gary, Ind.).

Variation in Processing and Physical Properties of Oil Masterbatches with Increasing Oil Content. W. K. Taft, B. G. Labbe and R. W. Laundrie (Government Laboratories, University of Akron, Akron, O.).

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY, DETROIT, MICHIGAN, MAY 4–6, 1955

The 67th Meeting of the Division of Rubber Chemistry was held in Detroit, May 4–5, 1955, with headquarters at the Hotel Sheraton-Cadillac. The meeting was attended by 1032 members and guests.

The 25-Year Club met under the Chairmanship of Mr. E. Kvet, with approximately 175 present. Due recognition was made of the fact that the meeting coincided with the 61st birthday of G. Allison. The contest for the longest service in the rubber industry was won by Bob Olin of the Olin Laboratories.

At the banquet, 637 members and guests were present.

At the Executive Committee meeting, the officers and directors established an award for the best paper presented at our National meetings. The committee in charge, subsequent to the meeting, selected the paper entitled, "Adriprene-B Urethane Rubber II. Factors Influencing Its Processability," by J. S. Rugg and G. W. Scott, as the best paper presented at the Detroit meeting. Due recognition of this honor will be given to the authors at the next meeting of the Division.

The Executive Committee created a new position in the Division, namely, that of Permanent Historian. The Chairman was empowered to select the person for this honor and, subsequent to the meeting, reported that he had received an acceptance from E. V. Osberg as the Permanent Historian of the Division.

The Executive Committee voted to consider the establishment of a new directorship in the Division, this directorship to be chosen from among the members resident in Canada. Final action, which will require by-law revision, will be taken at the fall meeting.

At the business meeting, recognition was made of the deaths since the last meeting of G. P. Loomis, L. L. Rydin, R. D. Abbott, G. S. Hiers, G. H. Glade, T. J. Kerr, C. A. Rackus, Gladding Price, and H. E. Simmons.

It was announced that the Charles Goodyear Medalist for 1955 is Ray P. Dinsmore.

The following papers were presented:

Effect of Temperature on the Air Permeability of Silicone Rubber. J. B. Gregory (Frederick S. Bacon Laboratories, Watertown, Mass.).

Evaluation of Silicone Rubber Modified with Teflon. W. H. Crandell (Frederick S. Bacon Laboratories, Watertown, Mass.).

Adiprene-B Urethane Rubber I. Properties of the Raw Polymer and Its Vulcanizates. F. B. Hill, C. A. Young, J. A. Nelson, and R. G. Arnold (Jackson Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Del.).

Adiprene-B Urethane Rubber II. Factors Influencing Its Processability. J. S. Rugg (Rubber Laboratory) and G. W. Scott (Jackson Laboratory, E. I. du Pont de Nemours & Co., Wilmington, Del.).

Profits. E. R. Bridgwater (E. I. du Pont de Nemours & Co., Wilmington, Delaware).

2-Methyl-5-Vinylpyridine Elastomers in Oil-Resistant Service. J. F. Svetlik, H. E. Railsback, and W. T. Cooper (Phillips Petroleum Co., Bartlesville, Okla.).

The Effect of Cure on Aging and Low-Temperature Properties. P. B. Stickney and W. J. Mueller (Battelle Memorial Institute, Columbus, O.).

Compounding Acrylate Polymers for Resistance to a Di-Ester Lubricant at High Temperatures. W. J. Mueller and R. A. Clark (Battelle Memorial Institute, Columbus, O.).

Reinforcement Studies of Synthetic Elastomers 1. The Effect of Mica Filler in Cured GR-S Rubber. G. W. Blum, A. Gaitan, and E. C. Bobalek (Case Institute of Technology, Cleveland, O.).

Reinforcement Studies of Synthetic Elastomers. II. Contributions of Carbon Black Reinforcing Effects to the Bonding of Butyl Rubber to Brass. G. W. Blum, T. J. Ling, and E. C. Bobalek (Case Institute of Technology, Cleveland, O.).

Reinforcement Studies of Synthetic Elastomers. III. The Mechanisms of Reinforcement: The Influence of Particle Size and Type on Tensile Behavior. G. W. Blum, S. M. Skinner, T. H. Ling, and E. C. Bobalke (Case Institute of Technology, Cleveland, O.).

Oxygen-Containing Groups on the Surface of Carbon Black. M. L. Studebaker, L. G. Nabors (Phillips Chemical Co.), E. W. D. Huffman (Huffman Microanalytical Laboratories) and A. C. Wolfe (University of Akron).

Abrasion of Butyl Rubber. R. L. Zapp (Standard Oil Development Co., Linden, N. J.).

Low-Temperature Evaluation of Tires. C. F. Dandareau, Jr., and C. W. Banton, Jr. (Detroit Arsenal, Center Line, Mich.).

Educational Activities of Rubber Groups. H. L. Fisher (University of Southern California and the Los Angeles Rubber Group, Inc.).

Chain Scission in the Oxidation of Hevea. I. E. M. Bevilacqua (United States Rubber Co., General Laboratories, Passaic, N. J.).

Chain Scission in the Oxidation of Hevea. II. E. M. Bevilacqua (United States Rubber Co., General Laboratories, Passaic, N. J.).

Emulsion Polymerization of Chloroprene. III. Molecular Weights and Film Vulcanizate Properties. Maurice Morton and Irja Piirma (University of Akron, Akron, O.).

Practical Rubber Vulcanization through Peroxide Cross-Linking. L. O. Amberg and W. D. Willis (Hercules Experiment Station, Hercules Powder Co., Wilmington, Del.).

Peroxide Cures of Nitrile Rubber. C. H. Lufter (B. F. Goodrich Chemical Co., Avon Lake Experimental Station, Avon Lake, O.).

Petroleum Waxes for Protecting Rubber Compounds from Cracking. P. D. Sharpe (Socony-Vacuum Laboratories, Brooklyn, N. Y.).

A Study of the Reaction of Ozone with GR-S Rubbers. E. R. Erickson, E. L. Hill and R. A. Berntsen (Augustana Research Foundation, Rock Island, Ill).

Ozone Cracking of Elastomers. JAMES E. GAUGHAN (Research and Development Division, Detroit Arsenal, Center Line, Mich.).

Degradation of Oil-Extended Polymers in Presence of Metal Salts. J. M. MITCHELL, W. EMBREE, AND B. MACFARLANE (Polymer Corp., Limited, Sarnia).

Oil-Extended Alfin Polybutadienes. A. A. MORTON, JAMES R. CRITSER, EMANUEL SCHOENBERG, AND BRAM B. BOONSTRA (Massachusetts Institute of Technology, Cambridge, Mass.).

Non-Staining Oil-Extended Rubbers. R. L. PROVOST, E. I. BORG, J. L. PAIGE, W. W. WHITE, AND L. H. HOWLAND (Naugatuck Chemical Division, United States Rubber Co., Naugatuck, Conn.).

Equation Governing Stability of Oil Masterbatches. J. DUKE, W. K. TAFT, A. D. SNYDER, AND H. R. MOONEY (Government Laboratories, Akron, O.).

The Determination of Free Sulfur in Rubber Compounds, Using Triphenylphosphine. M. J. BROCK AND T. W. OSBORNE (Chemical and Physical Research Laboratories, Firestone Tire and Rubber Co., Akron, O.).

NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1954. (Vol. xviii.) Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W.1, England. $7\frac{1}{4} \times 9\frac{3}{4}$ in. 186 pp. Price: £1, 1s., 0d (approximately $3.00).—Again the rubber manufacturing industry should be grateful to the Institution of the Rubber Industry for another excellent report. Like the preceding editions, this latest one, covering 1954, is comprehensive in its coverage of the various branches of the rubber industry, each section being contributed by an outstanding expert in his field. Among the general subjects are the planting and production of raw rubber and latex, the chemistry and physics of raw and vulcanized natural rubber, synthetic rubber, compounding ingredients, fibers and fabrics, and testing equipment. Specific products include tires, belting, hose and tubing, footwear, mechanical goods, surgical goods, cellular rubber, hard rubber goods, flooring, and roads. As usual, excellent cross-referenced author and subject indexes are included. As pointed out in the foreword, these reports cannot be regarded in the light of bibliographies, but they do present a mosaic picture of the pattern of progress in the rubber manufacturing field. [From the *Rubber Age* of New York.]

SYMPOSIUM ON AGING OF RUBBER. Swedish Rubber Institute, P. O. Box 7310, Stockholm 7, Sweden. $8\frac{1}{2} \times 12$ in. Price: Sw. cr. 27 (approximately $5.25). (Mimeographed).—This is a compilaton of seven comprehensive papers delivered at the Symposium on Aging of Rubber at the Spring 1955 meeting of the Swedish Rubber Institute (Sveriges Gummitekniska Förening) in Karlstad. The papers were presented in English, German, Danish, and Swedish, and are reproduced in those languages in the bound volume.

Of the seven papers, four were delivered in English. These were: "The Significance of Accelerated Aging Tests", by G. W. van Raamsdonk, Rubber-Stichting, Delft, Holland; "Improved Methods of Laboratory Aging", by L. Bottomley, Monsanto Chemicals, Ltd., London, England; "The Effect of Antioxidants on Autoxidation in Light", by M. Davies and C. E. Kendall, Dunlop Research Center, Birmingham, England, and "Non-Staining Antioxidants", by G. E. Williams, Imperial Chemical Industries, Ltd., Manchester, England.

The other papers had the following titles: "The Mechanism of Deterioration of Rubber", by Holger Leth-Pedersen, A/S Nordiske Kabel; "An Antioxidant for Heat Resistance", by F. von Spulak, Farbenfabriken Bayer, A.-G., and "Various Factors in the Aging of Rubber", by Eugene Ganslandt, Trelleborgs Gummifabriks, A-G.

All the charts, graphs, and photographs utilized by the authors in their presentations are reproduced. [From the *Rubber Age* of New York.]

APPLICATIONS OF SCIENCE IN RUBBER TECHNOLOGY. Published by Dyestuffs Division, Imperial Chemical Industries, Ltd., Manchester 9, England. $7\frac{1}{4} \times 9\frac{3}{4}$ in. 101 pp.—Several years ago Imperial Chemical Industries issued a book on "The Fundamentals of Rubber Technology". This book contained eight lectures given by invitation during the 1946-47 session on rubber technology at the Newton Heath Technical School in Manchester. The current publication, which is complementary in nature to the first work, is based on a subsequent series of lectures at the same school. It contains five lectures, all concerning the applications of science in rubber technology, including: (1) General Introduction, by W. J. S. Naunton; (2) Chemistry and Rubber Technology, by J. T. Watts; (3) The Physical Sciences and Rubber Technology, by J. M. Buist; (4) Mathematical Statistics and Rubber Technology, by G. E. P. Box; (5) The Sciences and Rubber Growing, by E. J. McNaughton. As indicated in the preface, an approach rather different from that usually found in text books available to students of rubber technology is employed in the lectures, namely, the liaison between "pure" knowledge and its everyday application in the industry is systematically employed. This approach increases the practical value of the work. [From the *Rubber Age* of New York.]

EMULSION POLYMERIZATION. HIGH POLYMERS. Vol. IX. By Frank A. Bovey, Minnesota Mining and Manufacturing Co., I. M. Kolthoff, University of Minnesota, Avrom I. Medalia, Boston University, and Edward J. Meehan, University of Minnesota. Interscience Publishers, Inc., New York. 1955. xii + 445 pp. 16×23.5 cm. Price, $12.50.—The authors have done a magnificent job of assembling and correlating the tremendous volume of investigative work carried out during the war years and immediately thereafter largely under the aegis of the Office of Rubber Reserve. The book deals almost exclusively with the kinetics and mechanism of emulsion polymerizations, particularly styrene-butadiene (GR-S) systems, rather than with physical properties of the end products.

A striking feature of the topic organization is the excellent summarizing of the general features of each aspect of the polymerization process involving free radicals, which precedes discussion of that aspect applied to the particular case of emulsion polymerization. Taken together, these summaries comprise nearly 20 per cent of the volume. After 58 pages of general summary, separate treatment is given to initiating systems, chain-transfer agents, the role of the detergent, the over-all kinetics of the process, inhibition and retardation, and copolymerization. Literature coverage appears not to extend much beyond 1952. The authors make a valuable contribution in pointing out existing contradictions, and in many cases suggest further research so specifically that the reader wonders whether at least some of the points may not by now in 1955 be at least partially resolved. Chapters dealing with experimental techniques and with aspects of the practical formulation of recipes appears to be extremely useful.

The book is profusely illustrated with graphical data. Often, however, the legends are not fully adequate to indicate what conclusion results from them, and the reader must hunt in the text for explanation. Also, in many instances symbols for different types of points are almost indistinguishable. Apart from this feature the physical format of the book is good. Author and subject indexes are excellent. [From the *Journal of the American Chemical Society.*]

INTERNATIONAL RUBBER DIRECTORY: 1955. Published by Verlag für Internationale Wirtschaftsliteratur, GmbH. P. O. Box 108, Zurich 47, Switzerland. $6\frac{1}{2} \times 9$ in. 576 pp. $12.80.—The second edition of this international directory has been completely revised and considerably expanded. Data on rubber manufacturers in several additional countries not covered in the first edition are given, and the current edition now covers rubber manufacturers in seventy different countries. All of the countries are grouped by continent, and it is relatively easy to locate any group of manufacturers in any part of the world. The listings are arranged alphabetically by city and town within the countries, rather than alphabetically by company, but each listing indicates the type of rubber products being made. This information appears in English in most cases, as well as in German or French or Spanish. The Directory also includes sections devoted to German-English-French, English-German, French and French-German-English vocabularies. A buyers' guide for machinery, equipment, chemicals, raw materials, etc., is included. [From the *Rubber Age* of New York.]

THE STORY OF TIRE BEADS AND TIRES. Walter E. Burton. New York: McGraw-Hill Book Company, 1955. pp. 196 + xii. 37s.6d.—The words "The Story of . . ." commencing the title of a book, evoke expectations of fascination and instruction. This beautifully produced volume does not disappoint on either count. It is well printed on glossy paper and has clear drawings and good photographs to illustrate all the processes and products described in the text. It is by no means solely a popular book, however, and even the expert in the subject should find something of interest, as parts of it venture deeply into the technology of wire manufacture and tire building. Two useful items are the lists of British and United States patents at the ends of the chapters, and the fund of information about the physical properties and specifications of wires used in tires, scattered throughout the text in tabular form. The last chapter, although perhaps irrelevant, is nevertheless interesting because it is concerned with other uses of wire in conjunction with rubber.

This is probably the first book devoted wholly to that important part of the tire, the bead, and as such, appears to fulfill its purpose very well. The work was prepared under the sponsorship of the National Standard Company, Niles, Michigan, and it is claimed to be the story both of the tire bead, and of that company. Fortunately, the second story is not allowed to intrude too deeply into the first, and the book is, in the main, both readable and to the point. [From the *Rubber Journal* of London.]

CARBOXYLIC ELASTOMERS *

HAROLD P. BROWN AND CARLIN F. GIBBS

B. F. GOODRICH RESEARCH CENTER, BRECKSVILLE, OHIO

Carboxylic elastomers may be cross-linked by means of reactions of the carboxyl groups[1]. The literature contains references to the preparation of elastomeric copolymers containing carboxyl groups[2], but the preparation of such polymers for subsequent cross-linking involving the carboxyl groups has not been described. The surface hardening of nonelastomeric films through reactions involving carboxyl groups of the polymers[3] and preparation of diene copolymers of methacrylic acid and acrylic acid for use as adhesives of rubber to steel have been described[4]. This paper describes methods of preparing elastomers of controlled carboxyl content, the influence of these groups on polymer and vulcanizate properties, and the use of carboxyl groups for vulcanization.

PREPARATION OF CARBOXYLIC ELASTOMERS

Three methods for the preparation of carboxylic elastomers were used in this work. Unsaturated carboxylic acids of the acrylic acid type were copolymerized with olefins and dienes. Polymers containing groups such as esters, nitriles, amides, and acid chlorides convertible to carboxyl groups were hydrolyzed to carboxylic elastomers. Carboxyl-bearing molecules, such as β-mercaptopropionic acid, maleic anhydride, and unsaturated carboxylic acids of the acrylic acid type, were added to elastomers in latex and solvent and on a mill.

Unsaturated carboxylic acids of the acrylic acid type were copolymerized in a variety of emulsion-type recipes. It was found that polymerization in an acid-type recipe was essential to incorporation of significant amounts of the carboxylic monomers. An illustrative polymerization recipe is given in Table I. Emulsion systems have been preferred, but preparations were also made in solvents.

TABLE I

TYPICAL POLYMERIZATION RECIPE FOR PREPARATION OF CARBOXYLIC ELASTOMERS

Dodecylamine hydrochloride recipe

	Parts
Monomers	100
Dodecylamine (90% neutralized with HCl)	5
Aluminum chloride	0.2
Potassium persulfate	0.2
Sulfole B-8	0.4
Water	200
Temperature (° C)	30–50
Time, 6 to 25 hours for 75 to 90+% conversion	

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 47, No. 5, pages 1006–1012, May 1955. This paper was presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society in New York, September 15–17, 1954.

Unsaturated carboxylic acids of the acrylic acid type were employed as comonomers to introduce carboxylic groups into polymers. These included acrylic acid, methacrylic acid, sorbic acid, β-acryloxypropionic acid, ethacrylic acid, 2-ethyl-3-propylacrylic acid, vinylacrylic acid, cinnamic acid, maleic acid, fumaric acid, and several other polymerizable organic acids. The first three monomers were copolymerized with many olefins and diolefins, such as acrylic acid esters, methacrylic acid esters, styrene, acrylonitrile, methacrylonitrile, vinylidene chloride butadiene, isoprene, 2,3-dimethylbutadiene, and chloroprene. Several terpolymer systems yielded interesting elastomers, e.g., those which resulted from the copolymerization of acrylic-type acids with butadiene-styrene, butadiene-acrylonitrile, butadiene-vinylidene chloride, or butadiene-methacrylonitrile systems.

The amounts of carboxylic monomer incorporated varied widely with elastomeric materials, being prepared with as much as 0.3 equivalent of carboxylic monomer per 100 grams of rubber (ephr). For vulcanization or cross-linking purposes 0.1 equivalent of carboxylic comonomer was ample. As little as 0.01 equivalent of carboxylic comonomer could be readily detected in cross-linking reactions. Copolymers containing from less than 1 to over 98 per cent by weight of acrylic-type acid comonomers were prepared.

The polymerization systems were treated at the desired conversion with typical shortstopping agents, such as hydroquinone, and stabilizing agents, such as phenyl 2-naphthylamine or Stalite, before coagulation. The latexes were coagulated with reagents which ensured the preservation of the carboxyl groups of the elastomer as acidic groups. Thus the dodecylamine hydrochloride recipe was coagulated with hydrochloric acid, or methanol and acid. Calcium chloride solutions free of calcium hydroxide were also used.

The amount and distribution of carboxyl groups were controlled by the choice of comonomer acids, the monomer charging ratio, the conversion, the use of proportioning of one or more monomers, and the use of mixtures of acrylic-type acids.

In emulsion polymerizations with hydrocarbons such as butadiene, unsaturated carboxylic acid comonomers distributed themselves between the oil and water phases. The concentration of the unsaturated carboxylic comonomer in the oil phase, which is the probable locus of copolymerization, depended on the solubility of the acid, its charged concentration, and the influence of other components of the emulsion system on its solubility in water or oil.

Acrylic acid was more soluble in the water phase than in the oil phase. In the initial copolymer formed with butadiene, acrylic acid entered at a level about half that of its charged concentration. Polymer homogeneity was favored by proportioning butadiene, by use of acrylic acid levels higher than desired in the polymer, and by stopping the polymerization at moderate conversions (70 to 80 per cent).

Methacrylic acid had a higher oil phase solubility than acrylic acid. (For a charge level of 10 per cent by weight in the butadiene and dodecylamine recipe system methacrylic acid was 67 per cent and acrylic acid 13 per cent in the oil phase). In the initially formed copolymer with butadiene, it entered at a level about twice that of the charging ratio. Proportioning of the methacrylic acid favored more uniform polymer composition.

Because acrylic acid entered the butadiene copolymer at about half its charging ratio and methacrylic acid entered about twice as fast as its charging ratio, uniformity of carboxyl content of the copolymers was approached by the use of quantities of methacrylic and acrylic acids in proportions of about one to

two, respectively. This procedure was also effectively used in the preparation of carboxylic poly(ethyl acrylate), where the rate of polymerization was controlled by the rate of addition of the monomer charge to the emulsion system. A mixture of ethyl acrylate with acrylic and methacrylic acids in the desired proportion was employed, wherein equal weights of acrylic and methacrylic acids were used. The ratios of acids employed were empirically determined for each system.

Sorbic acid had a limited solubility in the butadiene and dodecylamine hydrochloride emulsion system (in contrast, acrylic and methacrylic acid were completely soluble). This limited the initial composition of butadiene with sorbic acid copolymers to a maximum of about 4.5 to 5.5 per cent of sorbic acid in the polymer. Because sorbic acid is a solid, control of polymer composition by proportioning of sorbic acid was difficult. To a certain extent excess sorbic acid in the system served as a gradually dissolving reservoir of monomer. Copolymers of butadiene and sorbic acid containing as much as 0.12 equivalent of sorbic acid were prepared.

In butadiene copolymer systems in the dodecylamine hydrochloride emulsified recipes, analyses of samples of 4 per cent or less conversion verified the preceding statements. Sorbic acid charged at levels of 6 and 10 per cent by weight gave 3.8 and 4.5 per cent, respectively, of sorbic acid in the initially formed polymers. Methacrylic acid charged at levels of 5 and 10 per cent by weight resulted in 10.4 and 20.0 per cent, respectively, of methacrylic acid in the initially formed polymer. Acrylic acid charged at levels of 5.3, 10, and 20 per cent gave 1.6, 4.2, and 11.3 per cent, respectively, of acrylic acid in the polymer.

Reactivity ratios could have been calculated for the butadiene-acrylic acid and the butadiene-methacrylic acid systems by correcting the charging compositions in terms of the oil phase composition of the emulsion system. However, the uncertainty of the polymerization locus and the possible effect of the emulsifier on the oil phase composition would render the calculations doubtful and of limited value. Although the reactivity ratios would have indicated approximate optimal charging compositions to provide polymer of desired carboxyl content, the actual compositions were readily selected empirically.

The initial charging of 0.1 equivalent (per 100 of monomers charged) of sorbic acid, methacrylic acid, or acrylic acid yielded polymers with butadiene which at 70 per cent conversion had carboxyl contents of 0.086, 0.116, and 0.049 equivalent, respectively. This corresponded to a nonuniform distribution of a carboxyl group for about every 83, 61, and 148 carbons or every 20, 15, and 36 butadiene units of the elastomer chain, respectively.

The butadiene-acrylonitrile-methacrylic acid system was prepared at a variety of charging ratios. In the system butadiene-acrylonitrile 55/45 the replacement of acrylonitrile by 0.015, 0.035, 0.05, and 0.174 equivalent of methacrylic acid yielded high conversion (80 to 95 per cent) polymer of 0.014, 0.036, 0.048, and 0.168 equivalent, respectively, for which low conversion (15 to 30 per cent) samples showed 0.021, 0.042, 0.045, and 0.171 equivalent, respectively. These data imply fairly uniform distribution of the carboxyl groups within these polymers. In the system butadiene-acrylonitrile 67/33, the replacement of acrylonitrile by 0.1 equivalent of methacrylic acid gave a polymer which at 4 per cent conversion contained 0.113 equivalent and at 72 per cent conversion 0.100 equivalent of methacrylic acid. Again the data indicated fairly uniform carboxyl distribution. However, in a low acrylonitrile system, such as butadiene-acrylonitrile 86.1/13.9, the replacement of acrylonitrile by 0.1 equivalent of methacrylic acid resulted in low conversion polymer (<5 per

cent) of 0.23 equivalent and a high conversion polymer (93 per cent) of 0.10 equivalent of methacrylic acid. Thus low acrylonitrile terpolymer systems behaved like the butadiene copolymers. Acrylonitrile content of the copolymers, verified by nitrogen analyses, was not significantly altered by the presence of the carboxylic monomers.

Poly(ethyl acrylate) copolymers in which various quantities of ethylacrylate were replaced by a mixture containing equal weights of acrylic and methacrylic acids were prepared by increment addition of the monomer mixture. The substitution of 1, 2, 4, 6, and 11 parts of the acid mixture for ethyl acrylate, corresponding to 0.0128, 0.0255, 0.0510, 0.0766, and 0.1408 equivalent of carboxyl, gave polymers which at 20 per cent conversion showed 0.012, 0.021, 0.044, 0.063, and 0.115 equivalent of carboxyl and at 90 per cent conversion had 0.012, 0.025, 0.051, 0.070, and 0.131 equivalent carboxyl contents, respectively. Thus polymers of fairly uniform carboxyl content were produced in this system.

The carboxyl content of elastomers was determined by titration with alcoholic alkali in appropriate solvents. For example, butadiene copolymers were commonly titrated with alcoholic alkali in benzene, butadiene-acrylonitrile copolymers in methylethyl ketone, and ethyl acrylate copolymers in benzene or benzene and ethyl alcohol. Many polymers showing gel in these solvents were found to be soluble in pyridine, which was a preferred analytical medium. Completely soluble polymers were titrated directly to a phenolphthalein end point. Samples containing gel were treated with a 50 per cent excess of alcoholic alkali (potassium hydroxide), shaken for 1 to 2 hours, titrated to disappearance of phenolphthalein pink color plus a slight excess, shaken another 1 to 2 hours, and titrated with alcoholic alkali to a pink color. (For high gel samples, or for polymers which precipitated during titration, the method was not analytically perfect, but the results were amply reliable for estimating amounts of crosslinking agents to be used.) The reliability of the analytical method was verified by carbon and hydrogen analyses on butadiene copolymers with methacrylic acid and with sorbic acid. Thus a butadiene-sorbic acid charged 94.4/5.6 of 84.5 per cent conversion possessed 87.70 per cent carbon, 10.96 per cent hydrogen, 0.145 per cent ash, and an oxygen content (by difference) of 1.29 per cent, which corresponded to 0.040 equivalent of carboxyl per 100 of polymer. Titration in benzene indicated 0.040 and 0.041 equivalent of carboxyl. Similarly a butadiene-methacrylic acid copolymer charged 88.8/11.2 of 92 per cent conversion contained 84.90 per cent carbon, 10.72 per cent hydrogen, 0.20 per cent ash, and an oxygen content (by difference) of 4.18 per cent, which corresponded to 0.1305 equivalent of carboxyl. Titration in methylethyl ketone gave 0.130 and 0.131 equivalent.

Latex hydrolysis was used as a method for preparing carboxylic elastomers from latexes of poly(ethyl acrylate), butadiene-ethyl acrylate, butadiene-methyl methacrylate, butadiene-acrylonitrile, and similar systems. One advantage of such latex hydrolysis preparations is that, because the original polymers do not contain free carboxyl groups, they may be prepared in alkaline-type polymerization systems employing common anionic soaps. In certain instances this method of preparing carboxylic elastomers may afford the use of comonomers having more favorable combining ratios than result when a corresponding hydrolyzed monomer bearing free carboxyl groups is employed. Solution hydrolysis of isolated polymers in selected solvents was also used.

The distribution of carboxyl groups in polymers derived by hydrolyses of carboxyl precursor groups in polymers, or by the addition of carboxyl containing molecules to polymer chains, may be very different from distribution ob-

tained by copolymerization. Acceptable carboxylic elastomers have been obtained by all three of these methods. Superior raw polymer properties and vulcanizates which have usually been observed for the emulsion copolymers may be attributable to a difference in carboxyl distribution.

RAW POLYMER PROPERTIES OF CARBOXYLIC ELASTOMERS

The physical properties of an unvulcanized carboxylic elastomer having a carboxyl content of 0.1 equivalent or less were essentially those of an analogous noncarboxylic polymer. The inclusion of increasing amounts of carboxyl groups in an elastomer elevated the temperature range of elasticity, increased the "nerve" of the polymer on the mill, increased the stiffness or brittleness, increased the crumb strength, imparted superior filming properties and strength to the polymer, increased the resistance of the polymer to swelling by hydrocarbon solvents, increased the susceptibility of the polymer to swelling by water, rendered the elastomer less elastic in its vulcanizates, and made the elastomer increasingly susceptible to cross linkage, gelation, and vulcanization by divalent ions.

The unsaturated carboxylic acid from which the carboxyl content was derived had very minor influence on the raw polymer properties or reactivity of the polymer toward divalent ions. Carboxylic elastomers of 0.1 equivalent or less carboxyl derived from acrylic acid, methacrylic acid, and sorbic acid were essentially the same.

The usual influence of modification on polymer plasticity, gel content, and molecular weight was observed in the carboxylic just as in analogous noncarboxylic elastomers. Thus polymers of low gel content and Mooney viscosities ML-4′-212° F of 50 to 60 handled easily on the mill, and more readily incorporated pigments such as black, zinc oxide, stearic acid, or phthalic anhydride than polymers of higher gel or Mooney values.

As the carboxyl level of carboxylic elastomers was increased above 0.1 equivalent, and particularly above 0.3 equivalent, the raw polymers became less and less elastic. A butadiene-methacrylic acid copolymer containing 0.377 equivalent of carboxyl was millable with difficulty on a 4-inch mill. Molded into a tensile sheet at 326° F under pressure for 20 minutes, the polymer showed an ultimate tensile of 3000 pounds per square inch at 365 per cent elongation. In contrast, most of the butadiene-carboxylic elastomers having 0.1 equivalent of carboxyl or less showed raw polymer ultimate tensile strengths of less than 100 pounds per square inch.

ROLE OF CARBOXYL GROUPS IN VULCANIZATION OF CARBOXYLIC ELASTOMERS

Sulfur vulcanizates.—Carboxylic elastomers were vulcanized in the recipes commonly employed for vulcanization of the analogous uncarboxylated elastomers. However, if polyvalent radicals and particularly divalent metals were available from the vulcanization recipe, the carboxylic groups influenced the vulcanization reaction. Scorchiness, increased moduli and tensile strengths, and sometimes decreased elongations, resulted. Stocks containing a metal oxide, such as zinc oxide, cured on the mill or on standing at room temperature. Monovalent salts such as potassium carbonate had a recognizable elevating effect on the moduli of the vulcanizates.

In the usual recipes of sulfur with Santocure, Altax, or Methyl Tuads, and similar recipes which include zinc oxide, the carboxylic elastomers cured at

room temperatures. However, the rate of cure was sufficiently slow to give reliable data when evaluation specimens were prepared immediately after mixing.

Metal salt vulcanizates.—The carboxyl groups of carboxylic elastomers make possible nonsulfur vulcanizations by means of reactions of the carboxyl groups, such as salt formation, esterification with polyhydric alcohols or diepoxides, amide formation with polyamines, and anhydride formation.

The reaction of a metal salt such as zinc oxide as a vulcanizing agent for carboxylic elastomers depends on salt formation between carboxyl groups in both inter- and intrapolymer reactions. Coordinate and ionic valences as well as hydrogen bonding are conceivably involved in the vulcanization. With polymers such as butadiene-sorbic acid and butadiene-acrylonitrile-methacrylic acid of 0.1 equivalent carboxyl content, gum tensile strengths as high as 11,000 pounds per square inch were obtained.

That zinc oxide and the carboxyl groups of the carboxylic elastomers interacted in vulcanization was indicated by the fact that both the level of zinc oxide and the carboxyl content of the polymer influenced the maximum tensile strength obtainable. Other observations have substantiated the salt formation concept. x-Ray examinations of butadiene-sorbic acid tensile sheets compounded with zinc oxide showed that zinc oxide disappeared during the vulcanization. A sample of butadiene-sorbic acid copolymer indicated by carbon and hydrogen analysis to contain about 0.048 equivalent of carboxyl was compounded with zinc palmitate in amounts of 2 to 33 parts per 100 of rubber and subjected to short-path distillation. The maximum amount of palmitic acid liberated was 0.041 equivalent. Essentially no additional palmitic acid was evolved when more than 12 parts of zinc palmitate per 100 of rubber was employed. A sample of this same polymer which had been vulcanized with 5 parts of zinc oxide per 100 was treated with carbon disulfide and dimethylamine, followed by a short-path distillation sequence which would remove all free zinc oxide as volatile zinc dimethyldithiocarbamate. Physical properties showed that devulcanization had not occurred. Polarographic determination of the residual zinc in the polymer showed 0.040 equivalent of zinc remaining in the polymer. Thus, an amount of zinc chemically equal to the carboxyl content of the polymer was chemically bound by the polymer.

Relatively small amounts of carboxyl groups have a significant influence on vulcanizate properties. The presence of as little as 0.01 equivalent of carboxyl was recognized in vulcanizates by elevation of tensile and modulus values. For vulcanization with divalent metals, a carboxyl content of 0.03 to 0.1 equivalent has been desirable. This corresponds to about one carboxyl for every 230 to 65 carbon atoms of the polymer chain.

Metal oxide vulcanizates of carboxylic elastomers showed unusually high tensile strengths, apparently superior ozone resistance, and ease of reclamation. The solvent resistance of metal oxide vulcanizates of polymers of 0.1 equivalent carboxyl or less was slightly better than that of sulfur vulcanizates of the corresponding polymers containing no carboxyl groups.

Adverse properties of the metal oxide vulcanizates were all related to poor stress retention or compression set. Thus metal oxide vulcanizates have shown low flex life in the DeMattia flex test, high compression sets, poor hysteresis, and rapid stress relaxation.

Monovalent salts impart a degree of "cure" or stiffening to carboxylic elastomers. The cure was less stable thermally than the cross-linkage developed with polyvalent metals. That monovalent salts imparted a stiffening effect

substantiates the idea that part of the vulcanization effect observed with divalent metals involves other than ionic cross-linkages. The following data illustrate the effect of a monovalent metal salt. A butadiene-methacrylic acid 91.4/8.6 copolymer (71 per cent conversion) having a carboxyl content of 0.118 equivalent when treated with 0.12 equivalent of sodium hydroxide, as a 2*N* aqueous solution, on the mill and molded for 20 minutes at 270° F had a tensile of 1700 pounds per square inch at an ultimate elongation of 900 per cent. The raw polymer possessed a tensile strength of <100 pounds per square inch without break under 1600 per cent elongation when similarly molded. This same polymer dissolved in ethyl alcohol, and treated with an equivalent amount of sodium hydroxide, gave a product which had the feel of a cured gum, and failed to mold to a smooth sheet, even at 360° F. The rough clear amber colored sheet gave an ultimate tensile strength of 1000 pounds per square inch at 155 per cent elongation. With zinc oxide, in contrast, tensiles of 6000 pounds per square inch at 400 per cent ultimate elongation were obtained.

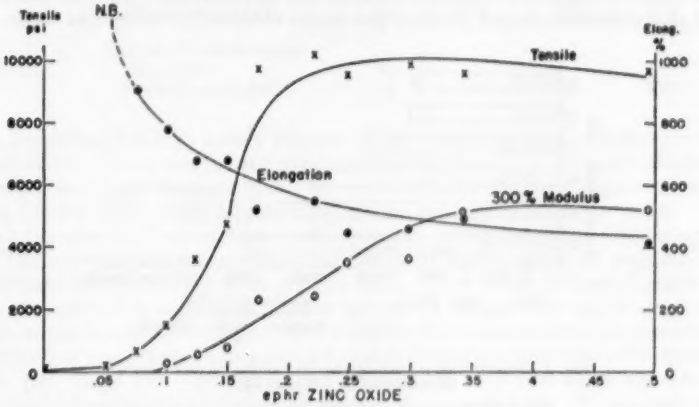


FIG. 1.—Influence of zinc oxide level on gum vulcanizates of butadiene-acrylonitrile-methacrylic acid.

55/35/10 copolymer of 73% conversion
0.099 equivalent of carboxyl per 100 rubber
0.05 equivalent pf phthalic anhydride used in all vulcanizates

While zinc oxide was extensively studied as a vulcanizing agent for carboxylic elastomers, the reactivity of several other metal oxides and salts was also demonstrated. Polyvalent metal salts of acids weaker than the polymer acid, or which yielded double decomposition products that volatilized or were otherwise removed from the polymer, served as vulcanizing agents.

When near theoretical quantities of the metal oxides were employed, the gum stocks approached transparency. Excess zinc oxide resulted in opacity. Some of the metal oxides, such as cadmium oxide, even when present in considerable excess, gave transparent or clear stocks. Optimal stress-strain properties were obtained by the use of about twice the theoretical amounts of zinc oxide or other metal oxides (Figure 1).

Zinc oxide vulcanizates of carboxylic elastomers were stable toward boiling water, 10 per cent sodium hydroxide, or 10 per cent sulfuric acid, and showed no deterioration in stress-strain properties after 24 hours.

Carboxylic elastomers mixed with zinc oxide or other metal oxides cured at room temperature in 48 hours or less. Zinc oxide stocks were scorchy on the mill. Organic acids, organic acid anhydrides, silica, boric acid, amines, and similar reagents were found to be retarders and controllers of the reaction of metal oxides with carboxylic elastomers. Organic acids as controllers materially increased the ultimate tensile strengths of metal oxide vulcanizates and overcame evidences of precure, such as poor flow of stocks in the mold, roughness, and warped or misshapen vulcanizates. Among the actions of the controller organic acids the following probably occur: (1) devulcanization, followed by revulcanization, allowing more uniform distribution of the cross-linkages of the elastomer chains; (2) reaction with polymer-COOMOH groups to give polymer-COOMOOCR′, and (3) salt formation with unreacted metal oxide. Stearic acid has been a preferred organic acid controller for butadiene, butadiene-styrene, butadiene-acrylate, and ethyl acrylate-carboxylic elastomer systems (Figure 2). Phthalic anhydride has been a preferred organic acid controller for carboxylic elastomers containing acrylonitrile. That zinc stearate and zinc phthalate cannot produce the results obtained by using zinc oxide and

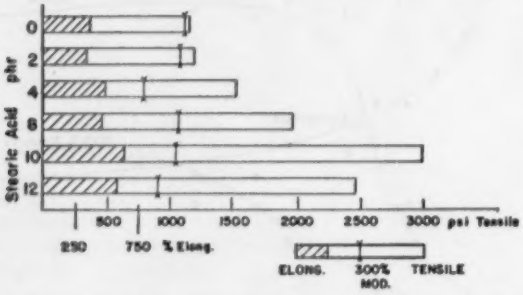


FIG. 2.—Stearic acid as controller for zinc oxide gum vulcanizate of butadiene-sorbic acid polymer.

0.04 equivalent of carboxyl per 100 rubber
9 parts zinc oxide per 100 parts rubber in all vulcanizates

the organic acid supports the proposed theories of mode of action of the controller organic acids. With a butadiene-sorbic acid 96/4 copolymer of 0.04 equivalent carboxyl and 9 parts (0.22 equivalent) of zinc oxide per 100, the use of 0.04 equivalent of palmitic acid, citric acid, phthalic anhydride, furyl acrylic acid, stearic acid, or succinic anhydride gave Mooney scorch times at 300° F in excess of 30 minutes compared with 2.7 minutes for zinc oxide alone.

Succinic anhydride was a particularly effective cure retardant in the carboxylic butadiene acrylonitrile system. Basic organic materials also acted as retarders of zinc oxide vulcanization, but no agents were more effective than phthalic anhydride, stearic acid, sebacic acid, and succinic anhydride.

Zinc-oxide gum vulcanizates of carboxylic elastomers exhibiting microtensile strengths of about 5000 pounds per square inch or less usually possessed increased moduli and tensile strengths indicative of reinforcement when carbon black was included in the vulcanizates. Carboxylic elastomer gum vulcanizates of higher tensile strength usually had increased moduli with reduced tensile strengths and elongations. The influence of 5, 10, 30, and 50 parts of carbon black (EPC, P33, SRF, HMF) and of equivalent amounts of clay, whit-

TABLE II

DEVULCANIZATION OF ZINC OXIDE VULCANIZATE OF CARBOXYLIC ELASTOMER AND ITS REVULCANIZATION

(Butadiene-methacrylic acid 91.4/8.6, 0.108 equivalent COOH, 78% conversion)

Sample	Description	Reagent (Parts/100 rubber)	300% Modulus (Lb./sq. inch)	Tensile strength (Lb./sq. inch)	Elongation (%)
A	Raw polymer		250	300	350
B	First vulcanization		—	5400	210
	Zinc oxide	11			
	Phthalic anhydride	4			
	EPC black	30			
C	Ground and remolded B	—	—	2350	180
D	Sample B with 1.5 theory oxalic acid	11	410	570	395
E	Sample D revulcanized				
	Zinc oxide	11			
	Phthalic anhydride	4	—	3700	260

ing, and silica in a high tensile polymer of the butadiene-acrylonitrile type was illustrative. Even the lowest pigment loading caused a decrease of tensile strength and slight increase in 300 per cent modulus values. The stress-strain data for the EPC black and whiting stocks were essentially the same. The black therefore did not increase tensile strength, but was merely a loading agent.

The metal oxide vulcanizates were readily devulcanized or reclaimed by treatment with an excess of an organic acid. Thus an elastic metallocarboxylate was ground to a crumbly mass or powder on a tight mill, and then an acid such as stearic acid incorporated on the mill until a smooth plastic mass resulted. Addition of more metal oxide and a suitable curing cycle restored the vulcanizate (cf. Table II). Complete devulcanization of a zinc-oxide vulcanizate required a theoretical equivalent or more of the organic acid. In the case of an acid of high molecular weight, such as stearic acid, an equivalent weight amounted to 70 parts per hundred for a 0.1 equivalent carboxylic polymer. Dibasic acids or polybasic acids, however, could be used. For example, about one-sixth as much oxalic acid as stearic acid was required, 11 parts per 100 being effective.

Polyamine vulcanizates.—Polyvalent organic radicals as well as polyvalent inorganic radicals can cross-link carboxylic elastomers. Hexamethylenediamine (1,6-hexanediamine) and other polyamines were used to cross-link carboxylic polymers. Both inter- and intramolecular reactions between the diamines and the carboxylic elastomer undoubtedly occurred. The intermolecular or primary cross-linkages probably were a dominant factor in the vulcanizate properties. However, secondary linkages resulting from intramolecular reactions, especially in the salt-forming stage of the reaction, undoubtedly contributed an effect. The carbonate of hexamethylenediamine was preferred, because this salt is less scorchy in compounded stocks than the free diamine and is easiler to handle on the mill. Milling at about 120° F sufficiently removed liberated carbon dioxide to avoid porosity in the cured stocks.

Stress-strain and compression set data indicated that there were two stages in the vulcanization of carboxylic elastomers with hexamethylenediamine or its

carbonate. These probably correspond to salt formation and diamide formation. Hexamethylenediamine carbonate vulcanizates, when cured to the complete or diamide stage, possessed unusually good compression sets. The vulcanizates possessed lower tensile strengths, but much better compression sets than were obtained with zinc oxide or other metal oxides. In contrast to the metal-oxide vulcanizates, the hexamethylenediamine cures required black pigmentation for optimum stress-strain.

Combined sulfur and metal salt vulcanization.—Vulcanization of carboxylic elastomers with metal oxides may be superimposed upon sulfur vulcanizates, sulfur vulcanization may be superimposed upon metal oxide vulcanization, or the two vulcanizations may be carried out simultaneously. A compromise of properties results in all cases, wherein the tensile strength rise and properties related to compression set deteriorate with increased predominance of the metal oxide vulcanizate.

PROPERTIES OF VULCANIZATES OF CARBOXYLIC ELASTOMERS

Copolymers of butadiene with acrylic-type acids.—The stress-strain properties of polybutadiene were materially improved by the inclusion of acrylic-type acid

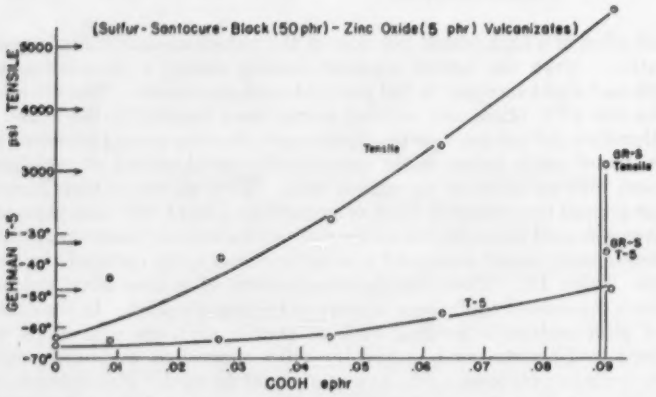


FIG. 3.—Dependence of tensile and Gehman values of butadiene-sorbic acid copolymers on carboxyl content.

comonomers, with only minor elevations of the low temperature characteristics as reflected by Gehman values. The effect was demonstrated in both sulfur vulcanizates with metal oxide and nonsulfur vulcanizates. In a sulfur vulcanizate with Santocure and zinc-oxide acceleration, the presence of 0.05 equivalent of carboxylic monomer gave stress-strain values approaching those of GR-S, while the Gehman values were 20° to 25° C lower (Figure 3). Both sulfur vulcanization and reaction of zinc oxide with carboxyl groups occurred. Polymers containing 0.1 equivalent or less of carboxyl possessed properties analogous to those of uncarboxylated polymers in nonzinc oxide-sulfur vulcanizates. In the zinc oxide-nonsulfur vulcanizates, those properties related to stress relaxation (flexure, compression set, hysteresis, etc.) were inferior to those of sulfur vulcanizates. The apparent superior ozone resistance of the metal oxide vulcanizates may be related to the high rate of stress relaxation.

Low gel contents, Mooney values of ML-4′ at 212° F 50 to 60, and conversions of about 75 per cent or less, gave polymers which handled well on the mill, and more readily incorporated pigments such as zinc oxide, stearic acid, and black than did higher Mooney, gel, and conversion polymers.

As a rule, the ultimate tensile strengths of the carboxylic polybutadienes were lower than those of carboxylic copolymers of butadiene with acrylonitrile. However, by selection of optimum conversion, gel content, carboxylic comonomer, and vulcanization conditions equally high tensile strengths have been obtained for the carboxylic polybutadienes. Thus a butadiene-sorbic acid 88.8/11.2 copolymer of 71 per cent conversion, showing 5 per cent gel in benzene and having a carboxyl content of 0.087 equivalent when vulcanized with zinc oxide (7 parts per 100) and evaluated without aging, had an ultimate tensile strength of 11,100 pounds per square inche at 575 per cent elongation with a 300 per cent modulus of 1560 pounds per square inch.

TABLE III

PROPERTIES OF CARBOXYLIC COPOLYMERS OF BUTADIENE

Comonomer acid	Methacrylic	Sorbic	Sorbic	None	GR-S
Carboxyl (ephr)	0.108	0.04	0.04		
Conversion (%)	78	84	84	50	72
Vulcanizate type	ZnO-gum	ZnO-gum	Sulfur	Sulfur-ZnO	Sulfur-ZnO
Recipe	A	B	D	C	C
Stress strain (ASTM) (300° F)	10 min.	40 min.	80 min.	60 min.	60 min.
300% modulus (lb./sq. inch)	2500	860	1900	340	100
Tensile (lb./sq. inch)	4000	3330	2560	1000	3080
Elongation (%)	380	625	245	535	545
Ozone (25 pphm, time to initial crack at 120° F, hr.)	213	5	0.17	0.5	1
Stress decay at 70° C (time for 20% decay, hr.)	0.03	0.034	1.1	13.5	85
Comp. set (22 hr. at 70° C) (%)	80	81	53	28	33
Tear (Graves)	27.5	15	11	18	20
Gehman					
T-5 (° C)	−37	−62	−52	−56	−36
FP (° C)	−58	−71	−58	−64	−42
Hardness (Durometer A)	82	72	58	52	56
DeMattia flex (100° F to 0.8 inch)	<100	<100	8000	56,500	36,500
Immersion (vol. increase in 7 days, %)					
Water at 100° C	4.7	2.7	4.0	21	37
Benzene at room temp.	310	420	300	370	340
CCl_4 at room temp.	380	520	350	490	400
Acetone at room temp.	16	12	19	11	22
Hexane at room temp.	116	170	130	141	106
Cyclohexane at room temp.	310		250	290	260

Recipe A*		Recipe B*		Recipe C*		Recipe D*	
Zinc oxide	12	Zinc oxide	9	Zinc oxide	5	Zinc oxide	10
Phthalic anhydride	4	Stearic acid	10	Santocure	1.2	Diphenylguanidine	2.5
				Softener	4	EPC black	30
				EPC black	30	Sulfur	1.5
				Sulfur	1.5	Pale paraffin-base oil	5

* Parts per hundred polymer.

For applications which require good low-temperature and stress-strain properties, without high flexing and low compression-set qualities, vulcanizates of carboxylic polybutadiene offer outstanding possibilities (cf. Table III).

Copolymers of butadiene and acrylonitrile with acrylic-type acids.—The substitution of methacrylic acid for acrylonitrile in the butadiene-acrylonitrile copolymer system resulted in virtually no change of the oil resistance of the polymers for amounts of methacrylic acid up to 0.15 equivalent. That carboxylic groups contribute oil resistance to diene copolymers has been mentioned by Marvel and coworkers[5]. The low-temperature properties as reflected

by Gehman T-5 freeze point values indicated that they are of the same order or slightly higher than those of a butadiene-acrylonitrile copolymer of the same butadiene content.

A zinc stearate-diphenylguanidine-sulfur vulcanizate of a carboxylic elastomer of 0.12 equivalent of carboxyl content was compared with a noncarboxylic butadiene-acrylonitrile elastomer of the same butadiene content in a sulfur-benzothiazyl disulfide stock with equal black loading. The carboxylic elastomer gave somewhat superior tensile strength, comparable solvent resistance, good ozone resistance, higher compression set, and poorer flex life. (It is possible that some zinc was derived from the zinc stearate by the carboxyl groups of the carboxylic elastomer.) A zinc-oxide gum vulcanizate of the carboxylic elastomer showed higher tensile strength, greater ozone resistance, comparable solvent resistance, higher compression set, superior tear, and poorer flexure properties than the sulfur-zinc stearate-black vulcanizate of the same polymer (Table IV). In pigmented stocks, the carboxyl groups caused elevated moduli, especially when the vulcanizate recipe included metal oxides.

Some potentialities for the use of combined metal oxide and sulfur cures were observed with low carboxyl content carboxylic elastomers of the butadiene-acrylonitrile system. After oil immersion, the vulcanizates of the carboxylic polymers possessed superior tensile strengths, without adverse effect on other properties.

Copolymers of butadiene and styrene with acrylic-type acids.—The substitution of methacrylic acid for styrene in butadiene-styrene copolymers resulted in increased tensile strengths and moduli with lowered elongations, increased hardness, poorer flex and hysteresis properties, and elevated Gehman low-temperature values in typical sulfur vulcanizates. In zinc-oxide gum cures, stress-strain properties equaling or surpassing those of GR-S in black-reinforced sulfur vulcanizates were obtained with carboxylic elastomers of the same butadiene content.

Copolymers of acrylate esters with acrylic-type acids.—Copolymers of several esters of acrylic acid with acrylic-type acids as well as terpolymers, including acrylonitrile, were studied. The behavior of the ethyl acrylate-carboxylic copolymers may be taken as typically illustrative of the effect of the carboxyl group on polymers of esters of acrylic-type acids. To provide polymers of good carboxyl group distribution, mixtures of equal weights of acrylic acid and methacrylic acid were used as the source of the carboxyl content of the ethyl acrylate polymers.

Copolymers of ethyl acrylate with methacrylic and acrylic acid, when vulcanized with zinc oxide, gave high gum tensile strengths. With increasing carboxyl content, the tensile strength rose, elongation dropped, and the Gehman value increased. The zinc-oxide gum vulcanizates possessed stress-strain properties equivalent to the best black vulcanizates with customary cures of Hycar PA or Hycar PA 21. The vulcanizates showed very poor compression set and related properties. Carbon black did not improve tensile strength of the zinc oxide vulcanizates, but at levels in excess of 10 parts per 100 of rubber, served principally as a diluent to the vulcanizate.

When copolymers of ethyl acrylate with acrylic and methacrylic acid were vulcanized with Trimene base in the recipe commonly employed with Hycar PA 21, increasing carboxyl level resulted in increased hardness, 300 per cent moduli, reduced elongation, improved compression set, and elevated Gehman T-5 value. Reaction was slightly slower with the carboxylic polymers than with Hycar PA 21.

TABLE IV

PROPERTIES OF CARBOXYLIC COPOLYMERS OF BUTADIENE–ACRYLONITRILE SYSTEM

Comonomer acid	None[a]	Meth-acrylic[b]	Meth-acrylic[b]
Acrylonitrile charged (phm)	45	35	35
% conversion	90+	90+	90+
Carboxyl (ephr)	—	0.12	0.12
% acrylonitrile by N analysis	41.2	32.6	32.6
Vulcanized type	Sulfur-ZnO	Sulfur-DPG	ZnO-gum
Recipe	A	B	C
Stress strain (ASTM) (300° F)	40 min.	40 min.	80 min.
300% modulus (lb./sq. in.)	860	2420	2840
Tensile (lb./sq. in.)	3250	4720	5500
Elongation (%)	610	430	410
Ozone (25 pphm), time to initial crack at 120° F (hr.)	12	21.1	142
Stress decay at 70° C, time for 20% decay (hr.)	3.1	3.1	0.046
Comp set (22 hr. at 158° F.) (%)	24	42	79
Tear (Graves)	20	18	27.5
Hardness (Duro-A)	65	60	84
Gehman test			
T-5 (° C)	−6	+2	+2
FP (° C)	−10	−2	−1
DeMattia flex at 100° F to 0.8 inch	122,500	4,000	1,500
Immersion, volume increase in 7 days, (%)			
Water at 100° C	3.2	3.6	10.6
Benzene at room temp.	160	116	160
CCl_4 at room temp.	57	48	57
Acetone at room temp.	220	170	230
Hexane at room temp.	4.1	4.2	4.1
Cyclohexane at room temp.	4.4	4.2	4.1

Recipe A	Phr	Recipe B	Phr	Recipe C	Phr
Zinc oxide	5	Zinc stearate	10	Phthalic anhydride	4
EPC black	30	Diphenyl-guanidine	2.5	Zinc oxide	12
Benzothiazolyl disulfide	1.25	EPC black	30		
Cumar	5	Sulfur	1.5		
Sulfur	1.25				

[a] Initially charged butadiene-acrylonitrile 55/45.
[b] Initially charged butadiene-acrylonitrile-methacrylic acid 55/35/10.

Hexamethylenediamine carbonate gave a faster and somewhat tighter cure with ethyl acrylate-methacrylic acid-acrylic acid copolymers than did Trimene base. The free diamine and aqueous solutions of the diamine were employed also, but the carbonate was preferred. Both the diamine and the carbonate reacted at or near room temperature to give polymer salts. The free diamine reacted more rapidly than did the carbonate. This salt formation caused a mild stiffening of the compound, which was more pronounced the higher the carboxyl content. For carboxyl contents below 0.05 equivalent, extrudability was not impaired. Gum vulcanizates cured to the second or diamide level

of cure were weak, but showed good reinforcement with carbon black and other pigments. Carboxylic poly(ethyl acrylates) prepared with an initial charge of 0.5 part each of methacrylic acid and acrylic acid (0.012 equivalent carboxyl), vulcanized with 1 part of hexamethylenediamine carbonate per 100, were contrasted at equal pigment loading with a Trimene-base vulcanizate of Hycar PA-21. They gave comparable stress strain, hardness, aging of stress strain and hardness, retention of stress strain at elevated temperatures, and similar reinforcement by blacks, whiting, and Hi-Sil. Equal or better De Mattia flexure, compression set; similar excellent ozone resistance, comparable Gehman values; comparable swell in ethyl alcohol, hexane, and benzene at room temperatures; similar swelling in ASTM No. 1 and No. 3 oils at 212° F; and superior resistance to boiling water (cf. Table V) were observed.

TABLE V

CARBOXYLIC POLYMERS OF ETHYL ACRYLATE VULCANIZED WITH HEXAMETHYLENEDIAMINE CARBONATE

Carboxyl content	0.047	0.022	0.012	None (Hycar PA-21)
ML-4′-212° F	50	55	59	46
Vulcanizate (phr.)				Trimene base 3
HMDAC[a]	3.76	1.8	1	Sulfur 0.5
Philblack-O	40	40	40	Stearic acid 1
		Wool grease 3	Stearic acid 1	Philblack-O 40
Stress-strain (ASTM) (cure cycle 80 min. × 320° F)				
Original				
300% modulus (lb./sq. in.)	—	1660	48	1550
Tensile (lb./sq. in.)	2150	2600	2200	1950
Elongation (%)	205	445	740	380
% Compression set[b]	50	46	62	36
Aged 4 weeks at 300° F in test-tube				
300% modulus (lb./sq. in.)	—	—	—	—
Tensile (lb./sq. in.)	1375	1210	800	420
Elongation (%)	50	120	210	285
% Compression set[b]	9	10	27	22
Gehman T-5 (° C)	+5	−2	−11	−6
De Mattia flex	<100	8000 to 0.8″	4,000,000 to 0.5″	1000 to 0.8″
Ozone wedge, 25 pphm, 20% stretch at 120° F (hr.)	NC[c] 164	NC 143	NC 167	NC 164
Immersion, volume increase in 7 days (%)				
H_2O at 212° F	9.8	10	40	89
ASTM No. 1 at 212° F	−0.9	3.6	0.7	−0.8
ASTM No. 3 at 212° F	7.8	10.5	10.7	10.0
Hexane	8.6	15.7	13	18
Benzene	143	254	433	251

[a] Hexamethylenediamine carbonate.
[b] % compression set after 22 hours at 100° C.
[c] No cracking.

Aminolysis is believed to have little or no part in the vulcanization of carboxylic poly(ethyl acrylate) with diamines. Poly(ethyl acrylate) was vulcanized with hexamethylenediamine. The reaction is believed to be one of aminolysis to produce diamide cross-linkages. Vulcanizates having properties similar to those of hexamethylenediamine vulcanizates of carboxylic poly(ethyl acrylate) have been obtained. Much higher levels of hexamethylenediamine and more severe curing cycles were required to vulcanize poly(ethy acrylate) than for carboxylic poly(ethyl acrylate). Hexamethylenediamine carbonate similarly could be employed, provided an agent such as stearic acid was included to promote the decomposition of the carbonate.

SUMMARY

Carboxyl groups can be introduced into elastomers by adding olefinic acids to suitable emulsion systems prior to polymerization. In general, such carboxyl groups elevate the elasticity temperature range, impart superior filming properties, increase resistance to swelling by hydrocarbon solvents, and render the polymers susceptible to cross-linkage, gelation, and vulcanization by polyvalent reagents.

In vulcanization recipes based on sulfur but containing polyvalent metal salts, the presence of as little as 1 per cent of a carboxylic monomer is recognizable through its influence on vulcanizate properties.

Carboxylic elastomers can be cross-linked by reactions of the carboxyl groups. Salt formation with zinc oxide, without pigmentation, gives stocks having stress-strain properties equaling or surpassing those of black-pigmented sulfur-cured vulcanizates of analogous noncarboxylic polymers. Several divalent metal oxides and other salts can be used as vulcanizing agents. The metal oxide vulcanizates possess excellent stress-strain properties, but poor compression sets. Certain vulcanizates are improved by the inclusion of small amounts of organic acids. An excess of organic acid causes devulcanization. Carbon blacks function principally as loading rather than reinforcing pigments.

ACKNOWLEDGMENT

The collaboration of A. E. Juve and L. O. Schroyer in vulcanization evaluations, of E. J. Carlson, Donald Druesedow, E. E. Gruber, and E. S. Pfau in polymerization studies, and of David Craig in the short-path distillation studies, is gratefully acknowledged.

REFERENCES

[1] Brown (to B. F. Goodrich Co.), U. S. Patents 2,626,248 (Jan. 20, 1953); 2,649,439 (Aug. 18, 1953); 2,662,874 (Dec. 15, 1953); 2,669,550 (Feb. 16, 1954); 2,671,074 (Mar. 2, 1954); 2,681,327 (June 15, 1954).

[2] Konrad and Bock (to I. G. Farbenindustrie A. G.), Ger. Pat. 667,163 (Nov. 1938); I. G. Farbenindustrie A. G., Fr. Pat. 842,186 (June 7, 1939); Semon (to B. F. Goodrich Co.), U. S. Pat. 2,395,017 (Feb. 19, 1946); Sauser (to B. F. Goodrich Co.), U. S. Pat. 2,395,506 (Feb. 26, 1946); McAlevy, Strain, and Chance (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,416, 060 (Feb. 18, 1947); Marvel, Fukuto, Berry, Taft, and Labbe, *J. Polymer Sci.* **8**, 599 (1952).

[3] Miller and Reid (to Firestone Tire & Rubber Co.), U. S. Pat. 2,604,668 (July 29, 1952).

[4] Frank, Kraus, and Haefner, *Ind. Eng. Chem.* **44**, 1600 (1952); *J. Polymer Sci.* **10**, 441 (1953).

[5] Marvel, Fukuto, Berry, Taft, and Labbe, *J. Polymer Sci.* **8**, 599 (1952).

BUTYL-TYPE POLYMERS CONTAINING BROMINE *

R. T. Morrissey

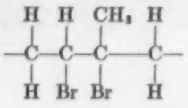
The B. F. Goodrich Research Center, Brecksville, Ohio

Butyl rubber has become well established as a useful synthetic rubber in industry. But despite its many unique properties, it has never developed beyond the status of a specialty rubber. Since its introduction in the United States, the major use has been in inner tubes. Other useful applications are believed possible through certain modifications of the Butyl rubber. The main properties in which improvement might be obtained are:

1. Rate of cure comparable to that of other vulcanizable rubbers.
2. Adhesion to other elastomers and metals.
3. Compatibility of cure with natural and synthetic rubbers.

The need for keeping Butyl stocks separated from other rubber compounds to prevent contamination has become a most important problem. This difficulty, along with its poor adhesion to metal, has greatly limited the uses of Butyl and eliminated it from consideration for many products in which its outstanding properties would be useful.

The bromine-modified Butyl polymers were discovered as a result of an intensive effort to improve these properties of Butyl rubber[1]. It was found during this study that the introduction of 1.0 to 3.5 per cent (by weight) of bromine along the Butyl polymer chain causes an appreciable increase of the vulcanization rate without affecting certain base polymer properties, such as air diffusion and ozone resistance. The reaction has been considered as mainly one of addition to the double bonds of the isoprene units contained in Butyl rubber so as to produce units of the structure



Although addition predominates, it is possible that some substitution of bromine does occur. It is postulated that the bromine present in the polymer is sufficient to saturate only part of the isoprene units, leaving the remaining units available for the curing of the polymer by sulfur.

If the modified Butyl polymer is considered as a whole, the polymer chains may be visualized as having the saturated and unsaturated isoprene units distributed randomly throughout the length of the chain. Therefore, there are available two principal types of curing mechanisms,—viz., the normal cross-linking, by means of sulfur and dehalogenation, and bonding through bivalent oxide exemplified by zinc oxide. As is well known, the oxide cure is completely ineffective in commercial Butyls. This double-cure mechanism present in the

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 47, No. 8, pages 1562–1569, August 1955. This paper was presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, New York, September 15–17, 1954.

brominated Butyl polymer likewise lowers the accelerator and sulfur requirements to approximately one-fourth to one-half the normal amounts used in Butyl.

GRI-17 POLYMERS WITH 2.5 TO 3 WEIGHT-PER CENT BROMINE HAVE FAST CURE RATE

Several methods of preparation have been employed in obtaining a useful polymer. Two of these processes are described.

The first method consists of preparing a solution of Butyl rubber in an appropriate solvent, such as benzene or heptane, and adding liquid bromine, usually in a solvent, to the Butyl cement. The modified Butyl may then be precipitated by mixing the brominated solution with a nonsolvent, e.g., alcohol. A variation of this method utilizes, as the solvent, an organic halogen compound that boils below room temperature, such as methyl or ethyl chloride. The resulting brominated cement may be run into hot water so that the solvent is flashed off and condensed while the polymer is coagulated. A portion of the bromine remains unreacted, and sufficient caustic is added to neutralize this excess. After allowing time for the completion of the neutralization reaction, a stabilizer, e.g., a slurry of calcium silicate, is added[2]. Zinc stearate or other protective agent may be added to the coagulating bath in order to prevent agglomeration of the crumb.

The second process involves adding an organic brominating agent such as *N*-bromosuccinimide or *N*-bromoacetamide to the Butyl polymer on a mill. The compound can then be heated in an oven at the decomposition temperature of the brominating agent for a sufficient time to allow completion of the reaction.

Obviously the properties of the brominated Butyl polymers are influenced to a certain degree by the precise method of introducing the bromine, and

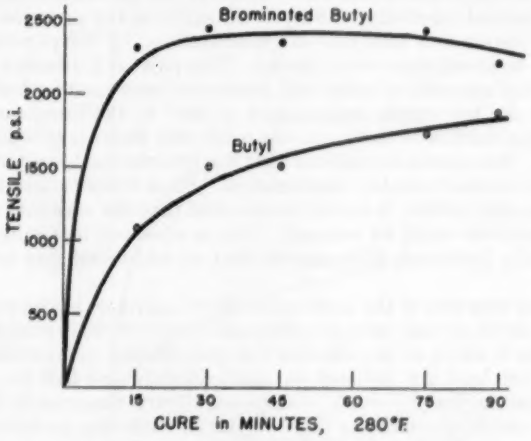


FIG. 1.—Comparison of cure rates of Butyl and brominated Butyl.

	Parts/100 parts rubber		
Nonoxidizing rosin	5.0	Ultramarine blue	0.2
Hydrated silica	39.0	TMTD	1.0
Zinc oxide	20.0	MBT	0.5
Titanium dioxide	15.0	Sulfur	2.0

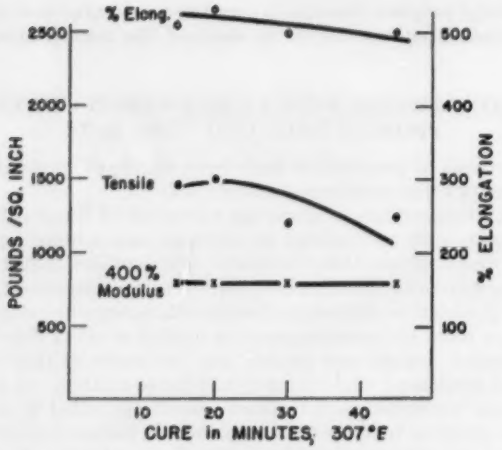


FIG. 2.—Stress-strain properties of brominated Butyl cured with 5 parts zinc oxide. Rubber, 100 parts; EPC black, 40.

different grades can be manufactured specifically to accentuate the various desirable properties.

The effects of bromination on the properties of Butyl are illustrated clearly by a comparison of the two polymers. The brominated polymers discussed in this study were made from GRI-17 and contained 2.5 to 3.0 per cent bromine by weight.

One of the major differences between Butyl and natural rubber or GR-S is the lower chemical reactivity of Butyl with sulfur in the presence of accelerators[3], which results in a slow rate of vulcanization. A Butyl which has been brominated, however, cures much faster. This point is illustrated in Figure 1. The customary amounts of sulfur and accelerator were used for both polymers, and even at the low curing temperature of 280° F, the brominated polymer reaches an optimum cure in 30 minutes, while the Butyl is still undercured in 90 minutes. It is generally believed that the low chemical reactivity of Butyl toward sulfur is due to its low unsaturation. Since bromination decreases the unsaturation still further, it would be expected that the cure rate obtained by the usual methods would be reduced. But as observed in Figure 1, the cure rate is actually increased; this suggests that an additional cure mechanism is involved.

The faster cure rate of the brominated Butyl polymers is also evident in the well-known curing system using *p*-quinone dioxime (GMF) in combination with red lead. As a result of bromination the quantitative requirements for both GMF and red lead are reduced to approximately one-half the customary amounts used in Butyl. Such brominated Butyl compounds have shown comparable tensile strengths to those of Butyl, while the modulus is doubled and the elongation is lower.

It has been found that the presence of bromine along the Butyl chains makes possible the development of a second entirely different method of cure which is not possible with Butyl. This type of cure is effected by the action of metal oxides, such as zinc oxide.

TABLE I

STRESS–STRAIN PROPERTIES OF BROMINATED BUTYL COMPARED TO BUTYL

Base Recipe

	Parts
Polymer	100.0
HAF black[a]	50.0
Zinc oxide	5.0
Oil[b]	10.0
Sulfur	2.0

	Brominated Butyl plus 0.75 part MBTS[c] and 0.20 part TMTD[d]			Butyl plus 0.5 part MBT[e] and 1 part TMTD[d]		
Cure at 280° F (min.)	300% modulus (lb./sq. inch)	Tensile (lb./sq. inch)	Elongation (%)	300% modulus (lb./sq. inch)	Tensile (lb./sq. inch)	Elongation (%)
30	1200	2250	500	325	2450	925
45	1500	2500	425	500	2650	765
75	1750	2700	425	700	2825	700
150	1800	2500	400	850	2700	625

[a] Philblack-O.
[b] Circosol-2XH.
[c] Benzothiazolyl disulfide.
[d] Tetramethylthiuram disulfide.
[e] 2-Mercaptobenzothiazole.

In the normal sulfur cure of Butyl, the presence of zinc oxide in Butyl is required for the proper activation of cure[4], and, as in natural rubber, it reduces the tendency toward reversion by reacting with the hydrogen sulfide to form zinc sulfide[5]. Nevertheless, Butyl cannot be cured with zinc oxide alone. The fact that fairly rapid cures can be obtained with only zinc oxide and EPC black in a brominated Butyl compound is demonstrated in Figure 2.

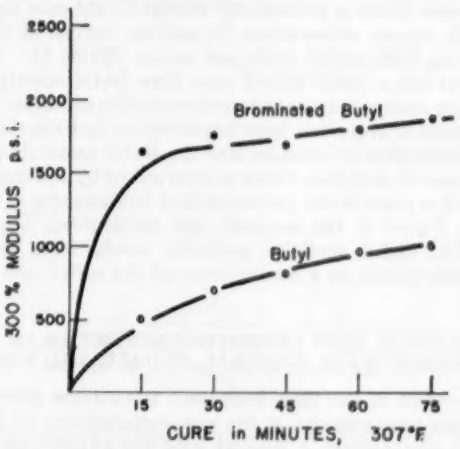


FIG. 3.—Comparison of modulus of Butyl and brominated Butyl.

	Parts/100 parts rubber		
EPC black	50.0	MBTS	0.5
Zinc oxide	5.0	TMTD	1.0
Stearic acid	3.0	Sulfur	2.0

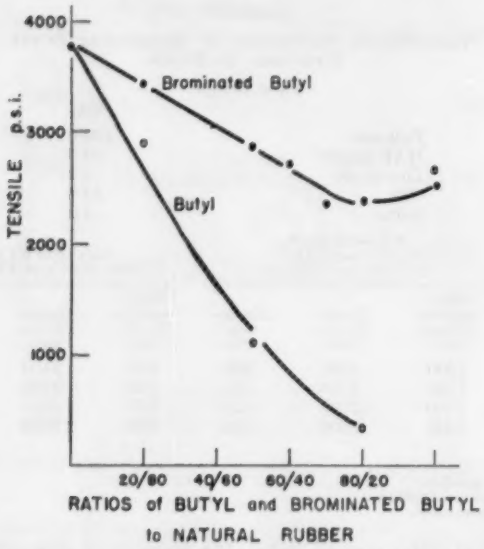


FIG. 4.—Effect of brominated Butyl on tensile properties of blends with natural rubber.

Parts/100 parts polymer-natural rubber			
Antioxidant	1.0	Oil	10.0
HAF	30.0	MBTS	1.0
Zinc oxide	5.0	DOTG	0–0.1
Stearic acid	1.5	Sulfur	2.0

The zinc oxide cure, which is presumably similar to the cure occurring in Neoprene[6], results in poorer stress-strain properties, compared to the combination cure involving both metal oxide and sulfur (Table I). It appears that brominated Butyl has a faster rate of cure than Butyl mainly because it has available two cure mechanisms that function simultaneously.

The low modulus of Butyl has been important in limiting the applications of Butyl. The introduction of bromine into the Butyl molecule produces a very substantial increase of modulus, which is determined by the degree of bromination and thus makes possible the preparation of vulcanizates of varying moduli. As indicated in Figure 3, the modulus can be doubled, approximately, by bromination. The higher modulus probably results from the accumulative cross-linking which occurs as a consequence of the sulfur and dehalogenation reactions.

BROMINATION ALSO IMPROVES PROPERTIES OF BUTYL BLENDS WITH NATURAL RUBBER AND GR-S

Stress-strain.—One of the most important advantages produced by bromination is the great improvement of the cure compatibility of Butyl with other rubbers. Every compounder is familiar with the admonition not to use any highly unsaturated rubbers or softeners with Butyl. Even as little as 1 to 5 per cent of these materials has been claimed to cause sponginess of cure[7]. It is this poor compatibility of cure with other elastomers that has limited the use of Butyl rubber in many desirable applications. A likely explanation

for the poor cure compatibility of Butyl lies in its very low unsaturation. It is believed that, in blends, the highly unsaturated polymers actually use all the curing ingredients, leaving nothing for the Butyl, which then acts merely as a softener.

Currently there is insufficient evidence to provide a complete understanding of the effects of bromination on the improvement of cure compatibility of Butyl with other elastomers. But here again the improvement seems to be due to the functioning of the double system of curing imparted by the brominated Butyl as already described, through the bromine by means of metal oxide and through the double bond by means of sulfur. Figure 4 indicates the superior qualities of mixtures of natural rubber with brominated Butyl, compared to mixtures with commercial Butyl. The tensile strength of Butyl is greatly lowered by relatively small amounts (5 to 30 parts) of natural rubber, and it is in this range that brominated Butyl contributes most to the improvement of the properties of such blends. Table II includes the stress-strain properties for two of the mixtures within this range.

The stress-strain properties of Butyl blends with the GR-S polymers are also greatly improved by bromination of Butyl. The data presented in Figures 5 and 6 show the increase in tensile strength which can be expected by the use of brominated Butyl as compared to Butyl in these mixtures. In the rosin acid GR-S (GR-S-1002), this increase is practically the same as for the blends with

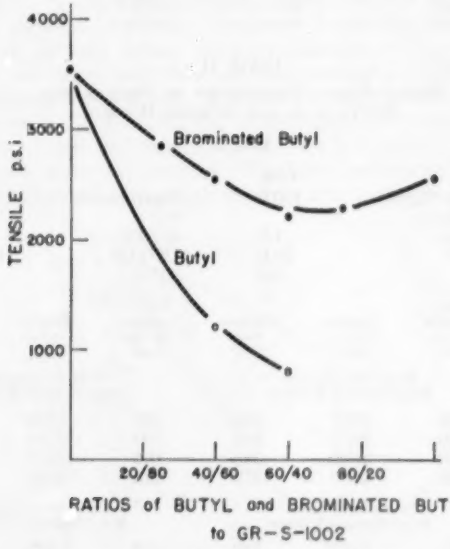


FIG. 5.—Effect of brominated Butyl on tensile properties of blends with GR-S-1002.

	Parts/100 parts polymer-GR-S-1002		
EPC black	47.5	*N*-cyclohexyl-2-benzothiazole sulfenamide	1.2
Antioxidant	0.3	(or) MBT	1.0
Stearic acid	1.5	DOTG	0.25
Softener	5.0	Sulfur	2.0
Zinc oxide	2.5		

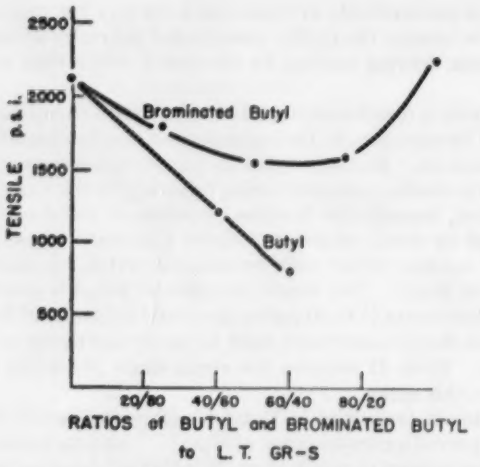


FIG. 6.—Effect of brominated Butyl on tensile properties of blends with low temperature GR-S.

Parts/100 parts polymer-l.t. GR-S			
Antioxidant	1.0	Oil	10.0
HAF	30.0	MBTS	1.0
Zinc oxide	5.0	DOTG	0.2
Stearic acid	1.5	Sulfur	2.0

TABLE II

STRESS–STRAIN PROPERTIES OF BROMINATED BUTYL–NATURAL RUBBER BLENDS

Recipe

	Parts		Parts
Brominated Butyl / Natural rubber	100.0	Stearic acid	1.5
Antioxidant[a]	1.0	Oil[c]	10.0
HAF black[b]	30.0	MBTS	1.0
Zinc oxide	5.0	DOTG[d]	0 to 0.1
		Sulfur	2.0

Cure at 280° F (min.)	300% modulus (lb./sq. inch)	Tensile (lb./sq. inch)	Elongation (%)	300% modulus (lb./sq. inch)	Tensile (lb./sq. inch)	Elongation (%)
	50:50 Brominated Butyl-Natural Rubber			60:40 Brominated Butyl-Natural Rubber		
15	500	2275	695	400	1900	695
30	750	2875	665	700	2725	655
45	800	2600	585	800	2625	595
75	900	2700	570	825	2485	560
	70:30 Brominated Butyl-Natural Rubber			80:20 Brominated Butyl-Natural Rubber		
15	375	1725	710	200	825	715
30	700	2380	615	525	2325	695
45	775	2130	525	615	2400	615
75	800	2175	530	700	2125	535

[a] AgeRite Stalite.
[b] Philblack-O.
[c] Circosol-2XH.
[d] Di-o-tolylguanidine.

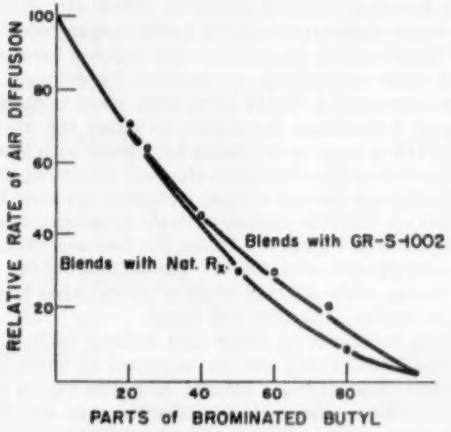


FIG. 7.—Effect of brominated Butyl on relative rates of air diffusion for blends with natural rubber and GR-S-1002.

natural rubber, ranging from two and one-half to five times. The difference is not quite so great for the mixtures with low temperature GR-S.

Air diffusion.—The low air-diffusion rate of Butyl[8] is well known, and this one property has been extremely important in establishing it as the leading polymer for use in inner tubes. The air diffusion of Butyl is not adversely affected by bromination, and therefore this excellent property can be imparted to other elastomers by blending. The relative rates at which the air diffusion of natural rubber and GR-S-1002 can be decreased by mixtures with increasing amounts of the brominated polymer are shown in Figure 7.

Ozone and flex-cracking resistance.—The low unsaturation of Butyl gives the polymer an undisputed advantage in its resistance to ozone[9]. It has often

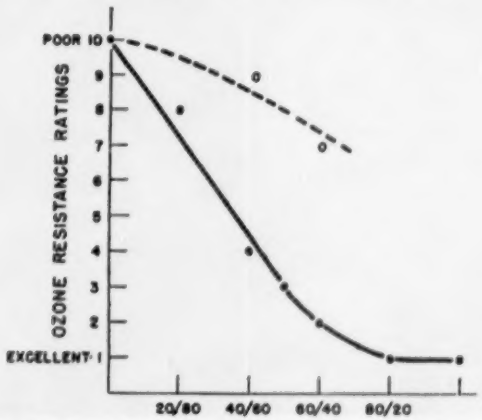


FIG. 8.—Effect of brominated Butyl on ozone resistance of blends with natural rubber of GR-S-1002. ○ Butyl/natural rubber blend. ● Blends of brominated Butyl with natural rubber of GR-S-1002.

been realized that blends of natural rubber or GR-S with Butyl-type rubbers having a superior ozone resistance should be useful in many applications. However, commercial Butyl cannot be used for this purpose because of incompatibility of cure with these elastomers, as mentioned previously. On the other hand, blends with brominated Butyl have been more successful. The solid line shown in Figure 8 indicates the degree to which the ozone resistance of natural rubber and GR-S may be increased by mixing with brominated Butyl. For comparison, the dotted line illustrates the poor results which were obtained with mixtures of Butyl and natural rubber. Further evidence for the improvement in ozone resistance which is possible with the brominated polymer is shown in the microphotographs in Figure 9. Under the test conditions of 25 p.p.h.m. of ozone, 20 per cent stretch, and 120° F, the natural rubber developed deep cracks in only 17 hours, while a 60:40 blend of brominated Butyl with natural rubber exhibited no cracks even after 150 hours.

The flex-cracking resistance of GR-S and natural rubber, which is closely associated with ozone attack, can also be improved by the addition of brominated Butyl. This is illustrated for natural rubber in Figure 10.

In order to obtain the maximum resistance to ozone and flex cracking, especially in the blends containing the lower amounts of brominated Butyl (10 to 50 parts), it is important to ensure an intimate mixture of the two polymers by mixing the natural rubber or GR-S into the brominated Butyl according to the following procedure:

1. Sheet out the natural rubber (mill rolls 170° F) or GR-S (cold mill).
2. Band the brominated Butyl polymer around the mill rolls at the recommended temperatures.
3. Make five separate additions of the natural rubber or GR-S, cutting it into the mix carefully after each addition.

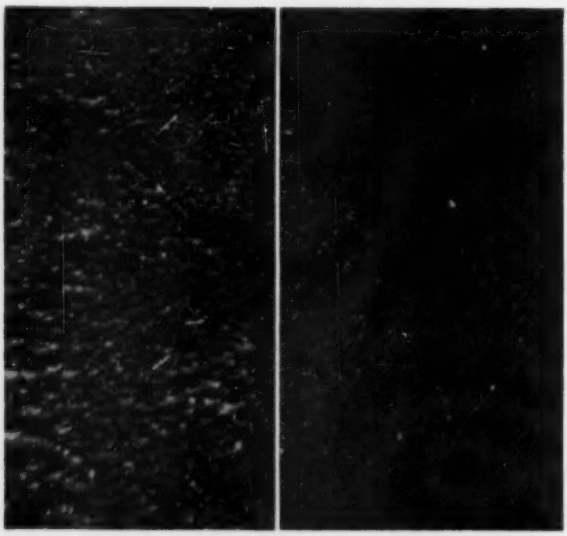


FIG. 9.—Effect of brominated Butyl on ozone resistance of blends with natural rubber. Ozone concn., 25 p.p.h.m.; temp., 120° F; elongation, 20%.

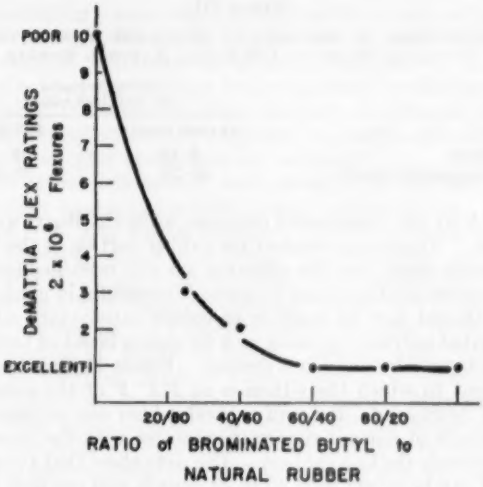


FIG. 10.—Effect of brominated Butyl on flex-cracking resistance of blends with natural rubber.

SATISFACTORY ADHESIONS BETWEEN BUTYL AND OTHER ELASTOMERS ARE POSSIBLE WITH BROMINATED BUTYLS

One of the main difficulties in the application of Butyl rubber to useful end products has been its poor adhesion to other elastomers. Many remedies for this have been tried with varying degrees of success. Hulswit and Wiechman[10] developed one of the first methods used extensively by the rubber industry. It involved the use of a cured Butyl tie-gum, one side of which was coated with a Butyl cement, the other with a cement of the other elastomer. The term tie-gum may be defined as a thin layer of rubber compounded specifically to adhere two noncompatible surfaces together. Doering and McCarroll[11] made a slight modification by introducing a layer of fabric instead of the tie-gum of cured Butyl. An important advance was made by the discovery that a small amount (10 to 30 parts) of a natural-rubber compound added to a partially refined cured Butyl would enable the resulting blend to be dissolved in ordinary rubber solvents[12], so that in many cases the tie-gum was no longer required. A method introduced by Wolf and Sparks[13] consisted of reacting a Butyl cement with sulfur monochloride. Following the completion of the reaction, the polymer was isolated, and the partially cured Butyl was compounded into a tie-gum stock, which was then sandwiched between Butyl and another elastomer. Mixtures of Butyl with other rubbers such as Neoprene and natural rubber have also been recommended as adhesive systems[14].

The poor adhesion of Butyl to other polymers is believed to be due to the same factors as is the poor cure compatibility of mixtures of the highly unsaturated polymers and Butyl. Most of the previous methods of adhesion have corrected this condition by first curing the Butyl. By employing brominated Butyl rubber this precuring step can be eliminated. As shown in Table III, an increase of 55 to 60 pounds per inch width at room temperature in the adhesion of Butyl to a GR-S and natural-rubber blend has been made possible by the bromination of Butyl. Still more important is the good adhesion which is re-

TABLE III

COMPARISON OF ADHESION OF BUTYL AND BROMINATED BUTYL TO BLEND OF GR-S AND NATURAL RUBBER

	Cooey adhesion (lb. pull/inch width)	
	At room temp.	At 212° F
Butyl	5–10	0
Brominated Butyl	60–70	20–30

tained at 212° F by the brominated polymer, while the Butyl without bromine has no adhesion. The composition of the rubber portion of the blend has been varied over a wide range, and the adhesion has still remained satisfactory.

Because brominated Butyl can be cured successfully in mixtures with other elastomers, it should now be possible to obtain satisfactory adhesion to any highly unsaturated polymer by using as a tie-gum a blend of brominated Butyl and the rubber to which adhesion is desired. Figure 11 illustrates this by indicating the extent to which the adhesion at 212° F of the brominated Butyl polymer to the mixture of GR-S and natural rubber can be improved by using increasing amounts of natural rubber in mixtures with the brominated Butyl as a tie-gum between the two rubbers. The data show that the strength of the bond at 212° F can be raised from 20 to 72 pounds pull per inch width by additions of natural rubber from 0 to 40 parts. The effect of the natural rubber on the adhesion at room temperature was only slight, increasing the value approximately 10 pounds pull per inch width over the concentration studied.

Since the brominated derivative of Butyl will adhere to the parent Butyl-type polymer as well as to the rubbers containing high unsaturation, it can be used as either a tie cement or gum to bond Butyl to these elastomers. It has been found that a 10 per cent heptane solution of brominated Butyl containing 40 parts channel black without curing ingredients can be used as the adhesive for

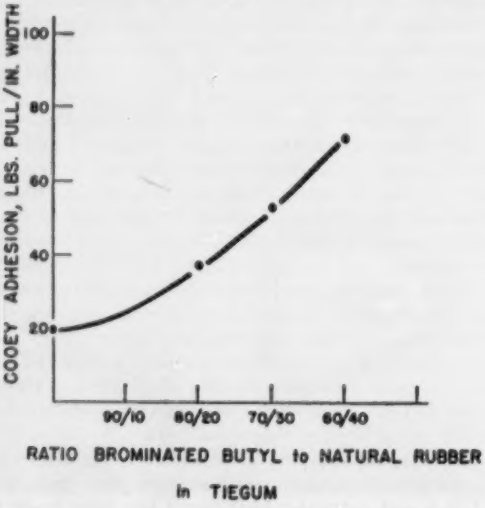


FIG. 11.—Effect of tie gum variation on 212° F adhesion to 50:50 GR-S-natural rubber.

this purpose, developing a bond strength of 30 to 40 pounsd pull per inch width. In testing such adhesives, observation of the type of bond failure is often important. For example, if the cement or tie-gum adheres to the Butyl rather than the natural rubber, the bond can be strengthened by adding small amounts of natural rubber to the tie-gum. Thus, through the versatile curing properties of brominated Butyl with other polymers, it is believed that most adhesion problems of Butyl to other elastomers can be solved.

The adhesion of Butyl to metals, particularly brass, has been an important problem. The main approach has been through compounding. High amounts of sulfur ranging from 3 to 4 parts have been reported as beneficial. Buchan[15] observed that increased loading in the form of carbon black or clay as well as the use of ultra-accelerators such as tetramethylthiuram disulfide (TMTD) were more important than high sulfur. Although chlorinated natural rubber has been used most extensively for rubber-to-metal adhesion, it has not been too successful in bonding of Butyl to metal. Ramsey and Petelin[16] have reported success in adhering Butyl to most metals by a Neoprene-AC cement containing phenolformaldehyde resin. More recently, Meyrick and Watts[17] have claimed that good adhesion to metal can be obtained by using a bonding agent consisting of chlorinated rubber dissolved in ethylene chloride, to which diisocyanate is added just before applying the cement to the metal surface. They also recommend high sulfur (4 parts).

It has been postulated that chlorinated rubber, an important component of many commercial adhesives, owes its bonding properties to the polar halogen, which reacts with both rubber and the metal surface, thus forming a chemical union of rubber and metal. A similar condition exists in brominated Butyl, where the polar bromine group is thought to be responsible for the good adhesion to metal. The work with chlorinated rubber has shown that the degree of rubber-to-metal adhesion depends on the amount of chlorine present in the polymer. The highly unsaturated natural rubber offers a very good opportunity for sufficient chlorination to take place, whereas the low unsaturation of Butyl does not allow bromination to a corresponding degree. Therefore, direct adhesion of brominated Butyl to metal is only fair. However, it may be greatly improved by coating the metal surface first with a phenol- or resorcinol formaldehyde resin. The polar groups present in the resin react readily with the bromine in the polymer, forming a chemical bond. In this type of assembly, a resin hardening solution is applied as a thin coat to the sandblasted metal surface, followed by a coat of a 10 per cent brominated Butyl cement.

Since brominated Butyl adheres to both Butyl and natural rubber, it has been found useful in bonding both types of rubbers to metal primed with

TABLE IV

ADHESION OF BUTYL STOCK TO RESIN-PRIMED METALS BY PIGMENTED BROMINATED BUTYL CEMENT

Metal[a]	Adhesion at 212° F (lb. pull/inch width)	
Copper	78	Stock failure
Brass	86	
Aluminum	87	
Stainless steel	100	
Magnesium	100	
Monel	90	
Zinc	90	

[a] All metals were sandblasted and primed with a phenol-formaldehyde resin solution.

TABLE V

ADHESION OF NATURAL RUBBER STOCK TO RESIN-PRIMED METALS BY PIGMENTED BROMINATED BUTYL CEMENT

Metal*	Adhesion at room temp. (lb. pull/inch width)	
Aluminum	119	(Stock failure)
Stainless steel	127	
Monel	107	
Magnesium	87	
Zinc	122	
Brass	124	
Steel	114	
Steel aged 1 wk. at 158° F	80	
Copper	130	
Copper aged 1 wk. at 158° F	63	(Bond failed)

* All metals were sandblasted and primed with a phenolformaldehyde resin solution.

phenol- or resorcinolformaldehyde resin. The problem is further simplified by the fact that the resin will adhere to practically any metal. As shown in Table IV, a Butyl curing bag compound was bonded to seven different metals—copper, brass, aluminum, stainless steel, magnesium, Monel, and zinc—by this method. In tests of these adhesions, the bond failure in almost every case occurred entirely within the Butyl stock itself, even when tested at 212° F. Under the same test conditions, no adhesion to the resin-primed metal surfaces was obtained without the brominated Butyl cement. A natural-rubber curing bag stock was adhered to the same metals using the same type of construction (Table V). Excellent room temperature adhesion was obtained in all cases, and bond failure always occurred within the natural-rubber stock. The exceptionally good aging characteristics of this bond are shown by the small drop in

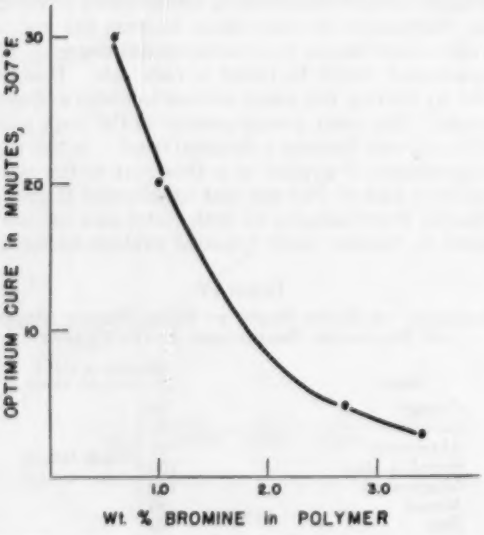


FIG. 12.—Effect of increasing amounts of bromine on cure rate of brominated Butyl.

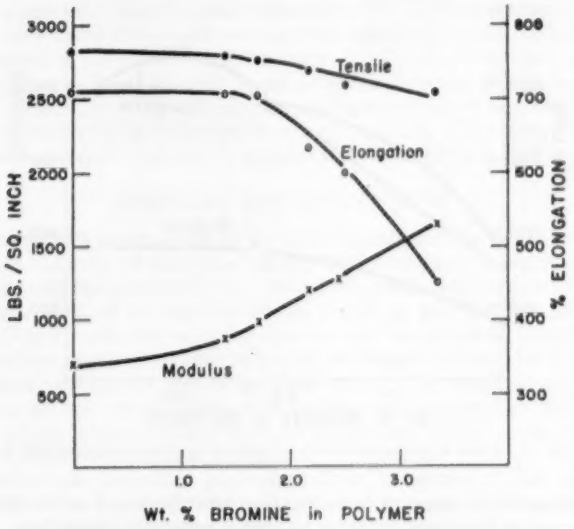


FIG. 13.—Effect of increasing amounts of bromine on stress-strain properties of brominated Butyl.

the adhesion value for steel after aging 1 week at 158° F. A strong bond of natural rubber to copper is normally difficult, especially one that will withstand prolonged aging at high temperatures. Table V shows the exceptionally good adhesion obtained between natural rubber and copper by using the brominated cement. Even after aging 1 week at 158° F, the bond strength was still approximately one-half as much as it was originally.

HALOGEN CONCENTRATION IS RELATED TO AMOUNT OF ADHESION

A study of the polymer at different bromine levels shows the extent to which the properties may be varied. Figure 12 indicates the rapid decrease of cure time resulting from increased bromine in the polymer. It is evident that the greatest change takes place when the halogen ratio is between 0.5 to 3.0 weight-per cent, the effect of additional amounts being very slight. Over the same range the tensile strength of the compounded polymer shows little change, except for the higher concentrations, which exhibit a 6 to 8 per cent decrease (Figure 13). The modulus rises gradually to more than double the original value.

The importance of the amount of bromine in the polymer on the cure compatibility with natural rubber is illustrated in Figure 14. The tensile strength rises practically as a straight-line function of the bromine content up to 2.5 per cent, from which point the properties tend to level out. This region of the curve indicates the optimum range of bromine concentrations. Investigations have shown that the mole-per cent unsaturation of the Butyl also plays an important part in determining the most satisfactory range of bromine concentration. Table VI shows the optimum ranges of bromine for three Butyl polymers of different unsaturation. Although there is some overlapping for the

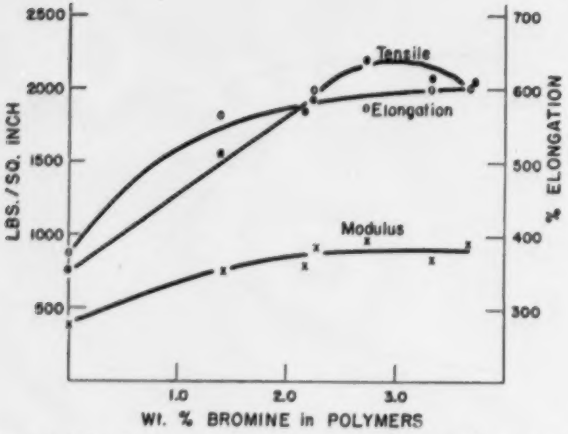


FIG. 14.—Effect of increasing amounts of bromine on stress-strain properties of 70:30 brominated Butyl-natural rubber.

various polymers, the range of concentration must be raised as the unsaturation of the polymer is increased, in order to obtain optimum properties.

TABLE VI

EFFECT OF PER CENT MOLE UNSATURATION ON OPTIMUM RANGE OF BROMINE CONCENTRATION

Percentage mole unsaturation	Optimum range of bromine (wt-%)
0.9	1.5–2.5
1.5	2.5–3.5
1.9	3.0–4.0

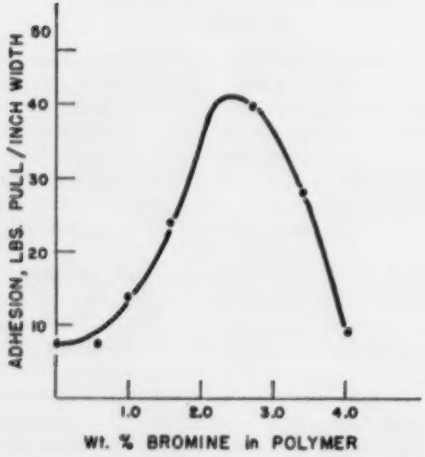


FIG. 15.—Butyl to natural rubber adhesion vs. bromine in adhesive polymer[1]

The evaluation of the adhesive properties of the polymer at various bromine levels has shown that the concentration of the halogen is important in determining the amount of adhesion which is obtained. This is particularly true when the brominated polymer is used as an adhesive between Butyl and another elastomer (Figure 15). The bromine required for maximum adhesion must also be adjusted to correspond to the degree of unsaturation. The various ranges for optimum bromine have followed in general the values given in Table VI.

SUMMARY AND CONCLUSIONS

Butyl rubber has been modified by attaching bromine to the polymer chain. The reaction has been considered as mainly one of addition to the double bonds, thereby lowering the unsaturation. Both sulfur and metal oxide can serve as vulcanizing agents for brominated Butyl, and both may function in the same compound, thus producing a faster rate of cure compared to Butyl. Brominated Butyl can also be covulcanized with natural rubber and GR-S, and therefore it is now possible to impart to these rubbers the excellent properties of Butyl, such as low air diffusion and resistance to ozone and flex-cracking. Still other advantages compared to Butyl rubber are higher modulus and good adhesion to other elastomers and metals.

Data have been presented to show that the properties of these new Butyl-type polymers can be varied by the amount of bromine which they contain. It has also been shown that there is an optimum range of the halogen concentration required for obtaining the best properties both in mixtures with natural rubber and in brominated Butyl polymers used as adhesives. This optimum range of bromine also depends on the original unsaturation of the polymer.

ACKNOWLEDGMENT

The writer wishes to acknowledge the helpful suggestions made by A. E. Juve, W. L. Semon, and D. M. Beach in the preparation of the manuscript.

REFERENCES

[1] Crawford and Morrissey, U. S. patent 2,631,984 (1952).
[2] Crawford and Morrissey, U. S. patent 2,681,899 (1954).
[3] Kemp, Malm, and Stiratelli, *Ind. Eng. Chem.* **36**, 109 (1944).
[4] Baldwin, Turner and Zapp, *Ind. Eng. Chem.* **36**, 791 (1944).
[5] Craig, Juve, Davidson, Semon, and Hay, *J. Polymer Sci.* **8**, 321 (1952).
[6] Catton, "The Neoprenes", E. I. du Pont de Nemours & Co., Wilmington, Del. **1953**, p. 5.
[7] Barron, "Modern Synthetic Rubber", Chapman and Hall, London, 2nd Ed. **1953**, p. 62; Chevassus, *Rev. gén. caoutchouc* **23**, 168 (1946); Enjay Co., "Butyl", **1948**, Sect. 1, p. 1.
[8] Chevassus, *Rev. gén. caoutchouc* **23**, 168 (1946).
[9] Ford and Cooper, *India Rubber World* **125**, 55 (1951).
[10] Hulswit and Wiechman, U. S. patent 2,392,590 (1946).
[11] Doering and McCarroll, U. S. patent 2,405,943 (1946).
[12] Morrissey and Crawford, U. S. patent 2,583,387 (1952).
[13] Wolf and Sparks, U. S. patent 2,442,068 (1948).
[14] Lightbown and Beekley, U. S. patent 2,467,322 (1949); Sarbach and Loomis, U. S. patent 2,541,550 (1951).
[15] Buchan, "Rubber to Metal Bonding", Crosby, Lockwood & Son, London, **1948**, p. 90.
[16] Ramsey and Petelin, *Rubber Age* (N. Y.) **65**, 541 (1949).
[17] Meyrick and Watts, *India Rubber J.* **122**, 505 (1952).

STUDY OF THE REACTION KINETICS OF AGING OF NATURAL RUBBER BY MEANS OF INFRARED SPECTROGRAPHY. III. EFFECT OF LIGHT AND INFLUENCE OF ANTIOXIDANTS *

V. Kellö and A. Tkáč

Chair of Physical Chemistry of the Slovak Technical High School in Bratislava, in Collaboration with the Cable and Insulator Research Institute in Bratislava, Czechoslovakia

In a preceding work the authors[1] studied the light aging of natural rubber under various conditions. The course of this aging was studied according to the curves expressing the relation of the increase of various functional groups (namely C=O, O—H) to the time. The increase was determined according to changes in the infrared spectra by a method published by the authors[2].

In technology, various materials are used to afford effective protection against the aging of rubber and rubberlike materials; these are generally called antioxidants. It is known, however, that many antioxidants are not effective against oxidation under all circumstances; they may have the opposite effect under different conditions. This difference is most pronounced in the different effect on raw and vulcanized rubber.

The effect of antioxidants depends to a large degree on the nature of the aging, that is, on whether the latter is caused principally by heat, light, or mechanical means. Various types of organic materials in which antioxidation effects can be assumed are discussed in this study. These measurements show that even small quantities of these substances, added to rubber, evidently influence the shape of the reaction curves; this attests to the fact that the reaction mechanism of light aging is very sensitive to these substances. Since their influence on the course of oxidation is very diverse and the concept of antioxidant often does not describe their true action, it is more accurate to divide them into inhibitors, retarders, and initiators of oxidation. As we will show later, this distinction can be made on the basis of the analysis of reaction curves of photocatalytic aging.

Blake and Bruce[3] observed that, in the action of light on raw rubber, most commercial types of antioxidants accelerate this type of oxidation. They also observed that an antioxidant currently in use, phenyl-2-naphthylamine, as well as di-2-naphthyl-*p*-phenylenediamine, are oxidation catalysts in unvulcanized rubber, although they inhibit oxidation in vulcanized rubber. According to Field, Woodford, and Gehman[4], phenyl-2-naphthylamine is ineffective in synthetic GR-S exposed to ultraviolet rays, although in this case, too, it is effective against heat aging.

The effectiveness of phenyl-2-naphthylamine during the heat aging of rubber was established by infrared spectography by D'Or and Kössler[5].

Stevens[6] studied the relation of tensile strength to the period of aging of rubber to which various antioxidants had been added. His measurements lead

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Chemické Zvesti*, Vol. 7, No. 7, pages 385–408, September 1953.

to the conclusion that antioxidants can be effective either from the beginning or not until the final phase of aging. Curve A in Figure 1 shows the relation of the tensile strength to the duration of aging in rubber without any antioxidant, curve B characterizes an antioxidant which is effective at the beginning, but less so toward the end, and curve C shows the influence of an antioxidant which is effective even in the later phase of aging. As we shall see later, our conclusions indicate the great variation in the effect of various substances at various phases of light aging.

The great importance of antioxidants in industry and agriculture certainly demands an explanation of the reasons for their effectiveness and the most accurate appraisal possible of these substances. From a theoretical viewpoint, it is necessary to study the causes of the varying effectiveness of different antioxidants. Although a large number of studies touch this problem, the theory of antioxidants is by no means complete yet, and needs to be supplemented by results obtained by all available methods.

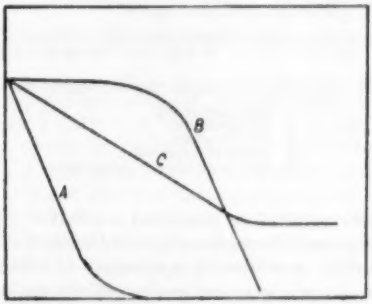


FIG. 1.—The abscissa represents the time of aging; the ordinate the tensile strength.

A. Without antioxidant.
B. Antioxidant effective at beginning.
C. Antioxidant effective in the later phase of aging.

PREPARATION OF THE TEST-SPECIMENS

Two per cent (by weight of rubber) of the antioxidant studied was dissolved in carefully purified benzene. When the material was only slightly soluble, a saturated solution was prepared. After agitation, the rubber was dissolved in this solution in such a quantity as to obtain a 0.5% solution. The subsequent procedure was published in the preceding study[2]. With one exception (tyrosine) all the measurements were made with the same mercury quartz tube. The distance of the apparatus from the specimen was 18 cm. (28° C).

RELATION BETWEEN REACTION CURVES AND CONCENTRATION OF ANTIOXIDANT

Since pyrogallol has proved to be one of the most effective antioxidants during photocatalytic aging, it was used for the study of the relation between the effect of the antioxidant and its concentration. Curves showing the relation between the increase of extinction of the absorption band ($C{=}O_{II}$ (1) and the exposure time (minutes in logarithmic scale) at equal concentrations of added pyrogallol are given in Figure 2. The curve for sheets of unextracted white crepe of approximately uniform thickness is designated by a dotted line.

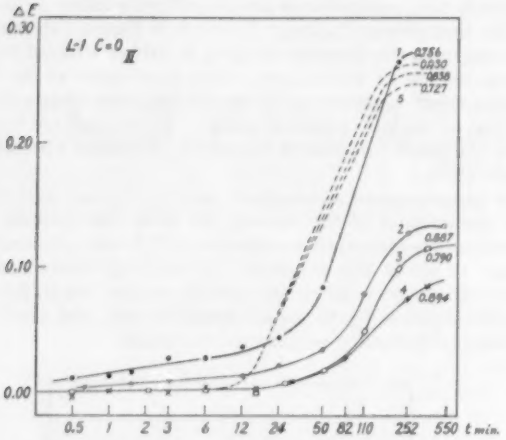


FIG. 2.—The abscissa represents time in minutes; the ordinate ΔE.

1. 0.2% pyrogallol.
2. 1% pyrogallol.
3. 2% pyrogallol.
4. About 4% pyrogallol.
5. Pale crepe without pyrogallol.

It is seen from the curves that an increased content of pyrogallol prolongs the initial induction period and lowers the curve in the stationary part. The slower increase of C=O groups is evidently a measure of antioxidation effect. The physical appearance of the specimens is also closely connected with the type of the curves; the sheets containing 0.3 per cent (of the rubber) or pyrogallol were sticky after 110 minutes of exposure and later became visibly cracked. The specimen with 1 per cent of pyrogallol was after a certain exposure less sticky, still slightly elastic, and the cracking was perceptible only through a microscope. The sheet containing about 4 per cent of pyrogallol, however, was still smooth and relatively elastic after 252 minutes. The relation between $\Delta E_{C=O}$ and the concentration of pyrogallol after exposure for 252 minutes is given in Figure 3. As is seen, the antioxidation effect of pyrogallol does not increase proportionally with the concentration, but reaches an optimal value at a definite concentration. Further increase of the concentration does not perceptibly increase the antioxidation effect. In order to establish the relation

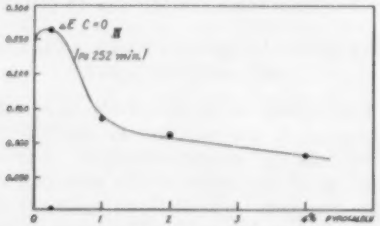


FIG. 3.—The abscissa represents the percentage of pyrogallol; the ordinate is $\Delta E_{C=O}$ after 252 minutes.

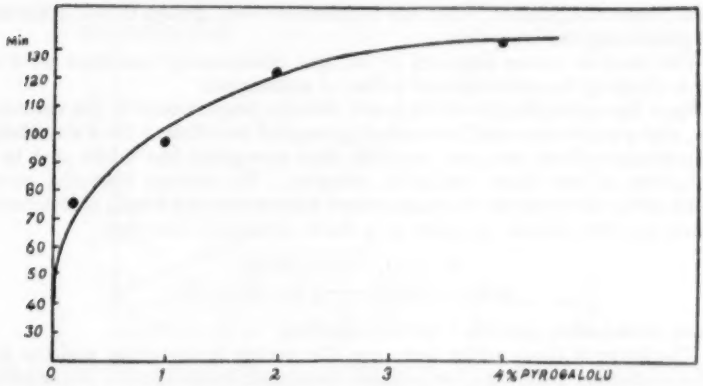


FIG. 4.—The abscissa represents the percentage of pyrogallol; the ordinate the time in minutes from 30 to 130 minutes.

between the antioxidation effect and the concentration by other criteria, we have characterized it in Figure 4 as the relation of a mean wave length time (the time when the curve reaches halfway on the rapidly rising middle part) to the concentration. It is seen here, too, that the curve reaches a certain maximum value, although it is not effective throughout the whole oxidation process, as is also shown by the value for a specimen with 0.2 per cent pyrogallol, where we observe a moderately accelerating increase of C=O groups in comparison with a pure specimen at the beginning of oxidation. The mean wave length time, then, can not be a satisfactory criterion of the effectiveness of an antioxidant.

The relation of the time in which $\Delta E_{C=O}$ reaches the value 0.040 (the beginning of the rapidly rising part of the curves, where we can assume a rapid deterioration of physical properties) and the concentration is depicted in Figure 5. We find a very good accord with Figure 3, which indicates that the antioxidant has its effect after the entire aging process. From all the diagrams it appears that the optimal concentration of pyrogallol is 1.5–2.5 per cent by weight of rubber. It is thus possible to characterize the effectiveness of antioxidants according to the form of the reaction curves, even if we assume that conclusive changes in the physical properties of rubber take place in the

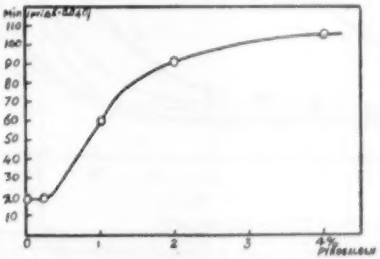


FIG. 5.—The abscissa represents the percentage of pyrogallol; the ordinate is the time in minutes from 20 to 110 minutes.

initial phase of oxidation, when the increase of C═O groups is still quite small and practically imperceptible.

The reaction curves obtained by infrared spectroscopy can then serve as a test in judging the antioxidation action of substances.

Since the antioxidation effect is not directly proportional to the concentration, and a relatively small amount of pyrogallol is sufficient for a considerable antioxidation effect, one can conclude that pyrogallol has taken part in the mechanism of the chain oxidation reaction. We assume that the varying height of the curves in the stationary part reflects varying length of the reaction chains, i.e., the number of cycles in a chain reaction of the type:

$$R\cdot + O_2 \longrightarrow ROO\cdot$$
$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

or one of the other possible types of reactions.

The fewer of these cycles there are, the weaker is oxidation, and the lower is the stationary part, which represents the dynamic equilibrium in the rubber-oxygen-antioxidant-oxidation byproducts—side-chain polymers system.

RELATION BETWEEN SHAPE OF CURVES AND PROPORTION OF ACCELERATORS OF OXIDATION AND ANTIOXIDANTS

Figure 6 shows the curves for rubber specimens containing mixtures of benzoyl peroxide and pyrogallol in 2 per cent by weight of rubber. The pro-

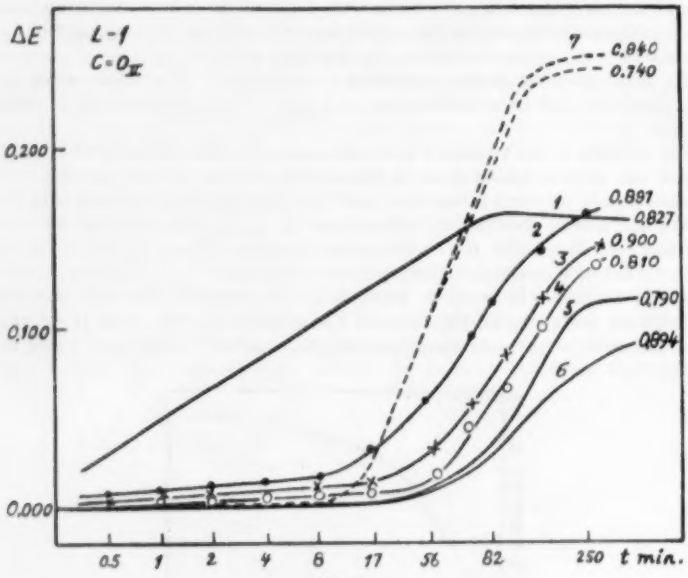


FIG. 6.

1. About 4% benzoyl peroxide.
2. Benzoyl peroxide + pyrogallol in ratio of 3:1 (2%).
3. Benzoyl peroxide + pyrogallol in ratio of 1:1 (2%).
4. Benzoyl peroxide + pyrogallol in ratio of 1:3 (2%).
5. 2% pyrogallol.
6. About 4% pyrogallol.
7. Pale crepe with no agent added.

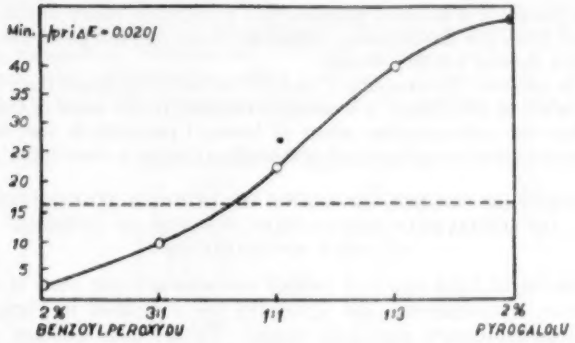


FIG. 7.—The broken line corresponds to the time when the specimen of pale crepe with no agent added reached the value of $\Delta E_{C-O} = 0.020$. The abscissa represents the proportions of benzoyl peroxide and pyrogallol; the ordinate is the time in minutes.

portion of benzoyl peroxide to pyrogallol was 3:1, 1:1, 1:3. The larger is the proportion of the antioxidant to the substance which readily forms free radicals, the lower are the reaction curves at the beginning, the longer is their gently rising part, and the lower is the stationary part. While the specimen containing about 4 per cent peroxide is oxidized rapidly, that containing peroxide and pyrogallol in the ratio 3:1 is oxidized considerably less rapidly; although still continually accelerating like the pure specimen, its stationary part is lower.

A mixture in the proportions 1:1 is an even stronger antioxidant and in the proportions 1:3 it has a good antioxidation effect.

These deductions can be seen clearly in Figure 7, where the relations of the time in which $\Delta E_{CO} = 0.020$ is reached, and the proportion of peroxide to pyrogallol are shown. Figure 8 gives a similar picture; here is given the relation of ΔE_{CO} to the proportion of mixture after exposure for 250 minutes. In all cases corrections were made for the unequal thickness of the sheets. All three sheets remained smooth and not sticky even after longer exposure. The appearance of rubber sol with the mixture containing different proportions of pyrogallol-peroxide is considerable. The solution containing the mixture 1:3 was the thickest and very yellow; that containing 1:1 was yellowish; and that containing 3:1 was thin and clear.

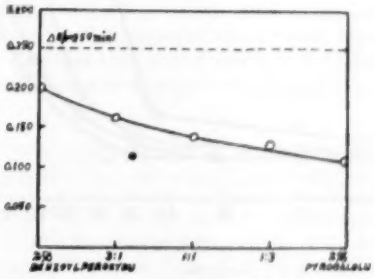


FIG. 8.—The curve represents the increase of ΔE_{C-O} after 250 minutes' radiation of pale crepe with no agent added. The abscissa represents the proportion of benzoyl peroxide to pyrogallol; the ordinate represents ΔE_{CO} after 250 minutes.

In the presence of benzoyl peroxide and pyrogallol, many initiation centers are formed from the decomposing peroxide; however, the more antioxidant is present, the shorter are the chains.

Since in all cases the stationary part of the curves is lower than in a rubber specimen without admixture, it is possible to state, in the sense of the preceding article, that the vulcanization effect of benzoyl peroxide is also observed in mixtures containing an antioxidant, although oxidation is considerably retarded.

RELATION OF COURSE OF AGING OF RUBBER TO COMPOSITION OF OXIDATION-REDUCTION SYSTEM OF RUBBER-OXYGEN-ANTIOXIDANT

The curves of light aging of rubber containing 2 per cent of *p*-quinone, quinhydrone, hydroquinone and pyrogallol are compared in Figure 9. The dotted curve represents pure pale crepe. We see that quinone accelerates

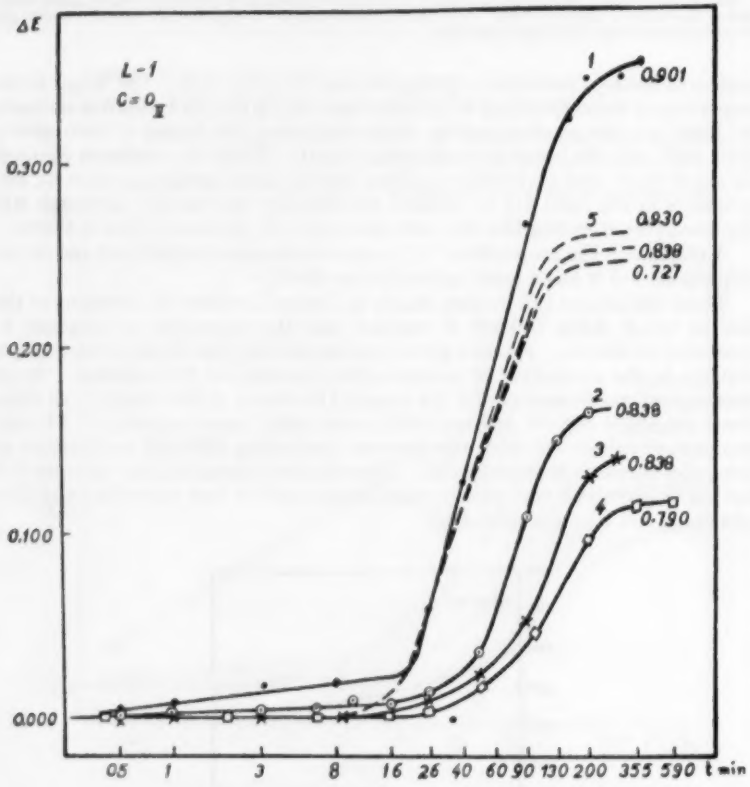
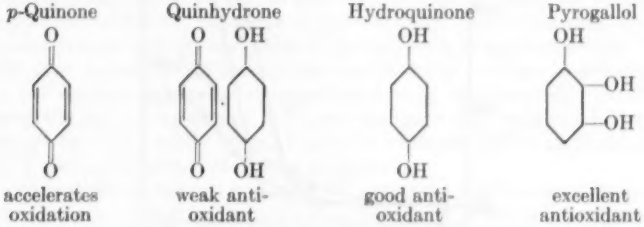


FIG. 9.

1. 2% p-quinone.
2. 2% quinhydrone.
3. 2% hydroquinone.
4. 2% pyrogallol.
5. Pale crepe containing no agent.

oxidation, while quinhydrone, hydroquinone and pyrogallol are progressively more effective antioxidants. If we compare the chemical formulas of the given substances, we see that, with the union of electropositive atoms of hydrogen to the molecule, the antioxidation effect increases. Consequently the initial slowly rising part of the curves is lengthened and the stationary part is lowered (scheme 1).



Although we do not know the value of the normal oxidation-reduction potentials for a given system in rubber, we can obtain certain information from a comparison of some experimental data. For example, the potential of a quinhydrone electrode with respect to a hydrogen electrode is 0.7044 V. The addition of quinone (0.005 mm.) increases this potential to 0.7570 V, and the addition of hydroquinone[7] lowers it to 0.6185 V. Thus the effect of completion of the reaction chains increases with a decrease of the oxidation-reduction potential of the antioxidants, i.e., with an increase of their oxidation capacity. This shortening of the reaction chains must appear in the curves as a lowering of the stationary part.

It seems that the mean value lies around 0.6 V. This value is designated by Bolland and ten Have[8] as the limiting value in the study of the oxidation of methyllineates in the presence of phenol antioxidants.

Semyonov[9] describes the nature of retardation of the oxidation chain reactions in the presence of pyrogallol. According to him, pyrogallol is one of the most effective inhibitors of oxidation reactions, for in contact with the peroxide radicals which appear in the development of the reaction chains, it easily transfers the hydrogen atom. Here a free semiquinone radical appears, which is unusually inactive. This agrees with the rule of Bagdasaryan[10], according to which, the more active is the molecule, the less active is its free radical. The slightly active radical can disappear through recombination more readily than react with isoprene polymers and thus initiate a reaction chain.

We observed clouding of rubber sheets after exposure in the presence of pyrogallol, similar to that which appears when water vapor comes in contact with the specimens. The fact that one of the final products during this mechanism of oxidation or antioxidation action of pyrogallol is water may serve to confirm this.

ANTIOXIDATION EFFECT OF DERIVATIVES OF PHENOL SUBSTITUTED IN VARIOUS POSITIONS

Rubber specimens to which 2 per cent of *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, and 1,2,4-dinitrophenol were added, were prepared. The solution with *p*-nitrophenol was fluid and clear; that with *m*-nitrophenol was thicker and clear; that with *o*-nitrophenol (with a chelate bridge) was a thick gel; and that with 1,2,4-dinitrophenol was a mobile yellowish solution.

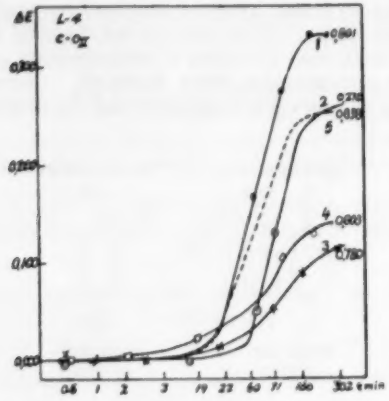


FIG. 10.—The abscissa represents the time in minutes.

1. 2% *o*-nitrophenol.
2. 2% *p*-nitrophenol.
3. 2% *m*-nitrophenol.
4. 2% 1,2,4-dinitrophenol.
5. Pale crepe containing no agent.

The sheets from the first three solutions were clear, and the latter was greenish. The curves of the relation of the increase of C=O groups to the time is shown in Figure 10. *o*-Nitrophenol, although almost ineffective in the initial phase, later begins to accelerate oxidation strongly (the sheet begins to crack badly, and later becomes very sticky); *p*-nitrophenol at first acts as a good antioxidant, but then oxidation takes place rapidly and in the stationary part even reaches the same degree as in the pure specimen. The sheet was cracked and unelastic. *m*-Nitrophenol acts as a very good antioxidant. After exposure for 350 minutes, the sheet was still smooth and somewhat elastic, although it remained yellowish brown. 1,2,4-Dinitrophenol at first accelerates oxidation slightly, and later it acts as a good antioxidant (the sheet was relatively smooth and remained brown). The shape of the reaction curves of increase of C=O groups with respect to time is compared with the simultaneous increase of OH groups in Figure 11.

If we study the relation between the values of the dipolar moments of *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol[11] and their effect on the rate of oxidation, or their antioxidation action, it is impossible to find a direct relation. *o*-Nitrophenol with a dipolar moment 3.10 *D* accelerates oxidation, *m*-nitrophenol with 3.90 *D* is an excellent antioxidant, and *p*-nitrophenol with 5.05 *D* at first acts as an antioxidant and then accelerates oxidation.

We can at least demonstrate a relation between the dipolar moment and the rate of the reaction[12]. A simple model of a dipole is a molecule composed of two independent ions. In reactions of ionic nature, in which the molecule does not participate as a unit, the molecule ionizes very rapidly, which requires ionization energy. Since the ions react practically instantaneously, the rate of this reaction depends on the rate constant of ionization k, which is given by the activation energy E_i: $k \sim e^{-E_i/RT}$. If we assume that in the beginning there were no ions present, then E_i is the ionization energy (which is equal to e^2/Dr). The larger is the charge of e ions, the smaller is their distance r and the smaller

is the dielectric constant D, then the more ionization decreases. Experiments have shown that these conditions, valid for pronounced ion compounds, can also be applied to nonpolar compounds of a dipolar character. Meerwien[13] studied the application of this theory to reactions in compounds where the passage of one substance into another is connected with a change of the dipolar moment of the compound as a result of the induction effect of strong molecular fields. These relations can not be so simple as in other types of reactions, because, in the compounds compared, the force of the electronic clouds between the individual polar groups and the elevation of the molecule is quite different. Consequently it is impossible to simply assume that the increase in the distance between the centers of gravity of opposing charges will inevitably result in a decrease of the activating energy. We can compare only such cases where the polar groups have an equally strong bond (for example, OH in carboxyl groups can not be compared with OH groups in phenol).

According to the equation: $k = \alpha_e^{-E/RT}$, where the rate constant depends on the steric factor α, as well as the activating energy, it is difficult to distinguish the influence of E and α on the rate constant k in the comparison of the experimental results. Furthermore, the action of the dipole on the activating energy will change according to the relation between the dipoles in the molecule. Detailed studies of the influence of substituents on the rate of reaction have shown that materials with substituents in *ortho*-position and *para*-position in a benzene nucleus behave more uniformly than substances with substituents in *meta*-position[14]. If the substituent is a halogen, the activating energy of *ortho*-compounds and *para*-compounds is less than in *meta*-compounds, while in nitro derivatives the situation is reversed: the activating energy of *meta*-compounds is less.

Our comparisons agree with the observation cited. Assuming that the antioxidation effect is conditioned by the appearance of a few active free radicals or their direct union with the rubber radicals, then as the chains are completed the most active of the three different nitrophenols is the *meta*-derivative, although its dipolar moment is not the largest (3.90 D). *o*-Nitrophenol, with the smallest dipolar moment, (3.10 D), in accelerating the oxidation of rubber,

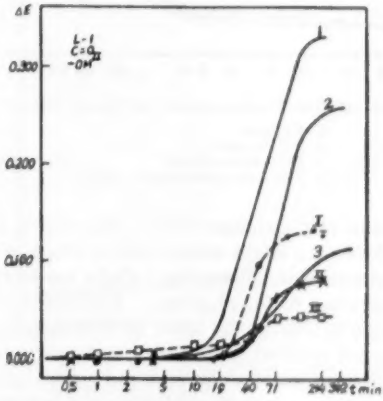


FIG. 11.—Curves 1, 2, and 3. Increase of C=O for *o*-, *p*-, and *m*-nitrophenol. Increase of OH for *o*-, *p*-, and *m*-nitrophenol. The abscissa represents the time in minutes.

probably forms as many reactive free radicals as *p*-nitrophenol, which has the largest dipolar moment and which, in the latter phase of the reaction, has a catalytic effect on oxidation. It is seen that, for an explanation of the relation between the rate of reaction and the dipolar moment, it is not sufficient to examine only the various tendencies in *o*-compounds, *m*-compounds and *p*-compounds, but it is also necessary to take into consideration the theory of "mean induced polarity"[15].

ANTIOXIDATION ACTION OF *o*-AMINOPHENOL

A benzene solution of pale crepe with 2 per cent *o*-aminophenol was prepared. A fluid yellowish sol appeared. Figure 12 shows the reaction curve of

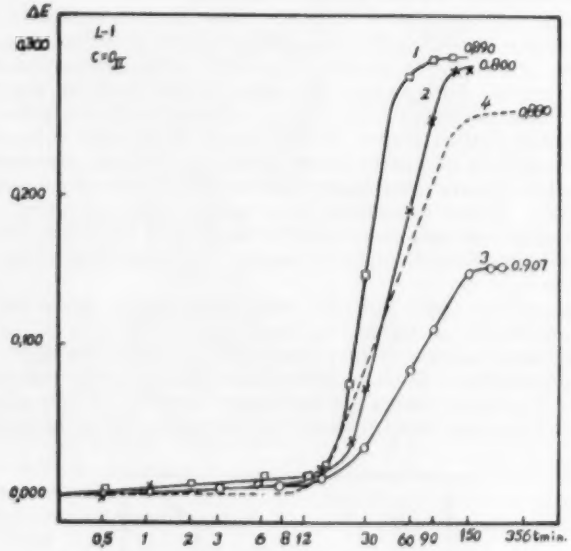


FIG. 12.—The abscissa represents the time in minutes.

1. 2% urea.
2. 2% thiourea.
3. 2% *o*-aminophenol.
4. Pale crepe containing no agent.

increase of C=O groups with exposure time. The curve, in comparison with the pure specimen, shows the slight antioxidation effect of *o*-aminophenol, although the initial segment of the curve has a slight tendency to rise, reflecting the weak initial acceleration of the reaction. The stationary part is considerably lower than in pure rubber. The sheet at first turned yellow and toward the end was smooth, not cracked, not sticky, and was still somewhat elastic. If the nitro group of *o*-nitrophenol is now replaced by the amino group, that is, if the electronegative substituent is replaced bythe electro positive one, the phenol derivative of benzene becomes an effective antioxidant.

INFLUENCE OF UREA AND THIOUREA

Sheets prepared from thick rubber solutions with 2 per cent of urea or thiourea were exposed. After about 180 minutes' exposure the sheets were cracked. The curve (Figure 12) in the specimen containing urea is analogous to that of pure rubber. However, after a turning point oxidation is rapidly accelerated.

If thiourea in which the oxygen is replaced by sulfur is added to rubber, we obtain a new type of reaction curve. At first we observe a moderate antioxidation effect, the initial phase of the curve is somewhat longer than in the case of pure rubber; then, however, a rapid acceleration of oxidation takes place. The height of the curves in the stationary part is approximately the same.

The primary amino group in the molecule alone is not enough to show an antioxidation action on the material. We shall see later that various mixtures can influence the course of the reaction in all possible ways.

EFFECT OF PHENYL-2-NAPHTHYLAMINE

Phenyl-2-naphthylamine is known as an effective antioxidant of vulcanized rubber. Blake and Bruce[3], state that this substance and similar types of current antioxidants accelerate the aging of rubber in light. With an increase of stickiness, they did not observe a considerable increase of the amount of oxygen absorbed. As the shape of our reaction curves shows (Figure 13), rapid oxidation takes place somewhat sooner in the pure specimen. It is significant, however, that the stationary segment of the curves is much lower, so that phenyl-2-naphthylamine in the later segment evidently acts as an antioxidant, and also shortens the oxidation chains and thus increases side-chain formation[3].

If phenyl-2-naphthylamine is exposed (one hour) before mixing, the initial phase is even shorter. Free radicals, which have relatively long life, then appear during the exposure of phenyl-2-naphthylamine.

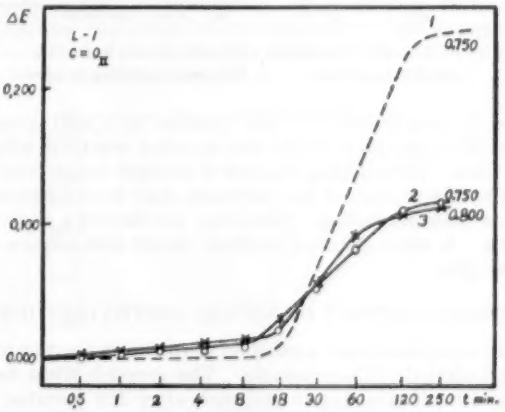


FIG. 13.—The abscissa represents the time in minutes; the ordinate ΔE

1. Pale crepe containing no agent.
2. 2% phenyl-2-naphthylamine which was exposed 1 hour under a mercury quartz tube.
3. 2% phenyl-2-naphthylamine.

EFFECT OF BENZIDINE

The curve of exposure of rubber to which 2 per cent of benzidine was added (Figure 14) shows a considerable lengthening of the initial phase, after which a short segment of more rapid increase appears. The stationary part of the curve is the lowest of all the cases observed yet. The sheet became yellow after exposure for 3 minutes; after 150 minutes it was yellow, smooth, and not sticky. The infrared spectra showed that the isoprene and vinyl structures were preserved. After 2000 minutes the sheet faded and remained smooth. The sheet was smooth and not sticky even after the end of exposure, that is, after 2200 minutes.

Blake and Bruce[2] regard benzidine as a typical retarder, since it greatly retards oxidation in light and prevents stickiness.

As a comparison of the physical properties and the course of the curve indicate, the number of C=O groups, although a good indication of the reaction mechanism of aging of rubber, is not a direct indication of the deterioration of the physical properties of the rubber in the initial phase of the curve, for this

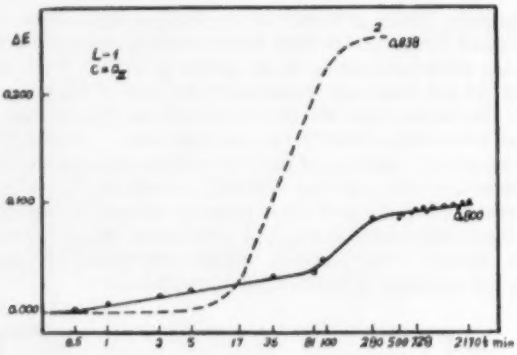


FIG. 14.—The abscissa represents the time in minutes.
1. 2% benzidine. 2. Pale crepe containing no agent.

deterioration is proportional to the number of C=O groups. The total deterioration of properties depends also on other reactions which may develop at the same time. For example, the loss of strength in the intial phase of oxidation, caused by the rupture of the polymers, may be compensated by a certain degree of side chain formation. However, we observe a slight increase of the C=O groups. A more detailed analysis would also require a study of the molecular weights.

ANTIOXIDATION EFFECT OF NICKEL DIETHYLDITHIOCARBAMATE

Sheets were prepared from a solution of rubber in a saturated benzene solution of nickel diethyldithiocarbamate. The greenish sheet was smooth after exposure for 90 minutes, began to crack after 210 minutes, and faded and grew sticky after 350 minutes. The curve in Figure 15 shows that the mixture is an effective antioxidant after about 60 minutes; later the curve rises rapidly and in the stationary phase it reaches about the same height as in pure rubber. The quality of the rubber then deteriorates after the initial effective interval.

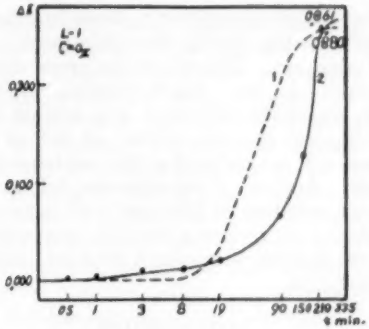


FIG. 15.—The abscissa represents the time in minutes.
1. Pale crepe. 2. About 1% nickel diethyldithiocarbamate.

Pinazzi[16] describes the good effects of nickel diethyldithiocarbamate (in quantity 1.5–2.5 per cent) as a protective material against light-aging of rubber. The compound which we used had not been previously appraised from this viewpoint, although by nature it is classed with those substances in which an antioxidation effect has been observed. As we stated, the antioxidation effect is reduced, with a loss of the original green color. We must, therefore, suppose that the course of light aging is a loss of nickel diethyldithiocarbamate either by decomposition due to the absorption of light or by direct combination with the rubber by radical reaction.

EFFECT OF TYROSINE

A sheet was prepared from a benzene solution of rubber saturated with tyrosine (about 0.5 per cent). The corresponding curve of the relation between the increase of C=O groups to the exposure time is given in Figure 16. Tyrosine greatly accelerates oxidation; this is reflected in the appearance of the sheet, which is very sticky after only 30 minutes. The curve is much higher than that of the pure rubber specimen in the stationary phase.

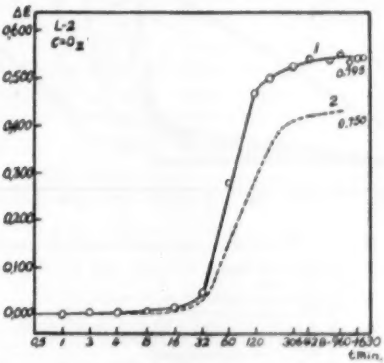


FIG. 16.—The abscissa represents the time in minutes.
1. About 0.5% tyrosine. 2. Pale crepe.

Tristram[17], by the analysis of proteins in Hevea brasiliensis latex, established the existence of these following, among other amino acids: glutaminic, asparagic, tyrosine, arginine, lyzine, etc. The role of the amino-acids present as natural antioxidants is generally known. Since tyrosine, which is also one of the amino-acids present, accelerates oxidation, it is evident that natural catalysts of oxidation can be present in crude rubber, as well as natural antioxidants. We can not now make a generalization that amino-acids act in general as effective antioxidants. Analysis of our experimental curves demonstrates well the cause of the great variation in the quality of natural rubber of even the same kind. Neither can we assume a uniform composition of natural oxidation-reduction systems in every elementary segment, either from a qualitative or a quantitative viewpoint.

CONCLUSIONS

As is evident from Figure 17, in which various types of curves are drawn, the action of individual types of chemical compounds can be quite diverse. This means that a substance can at the very beginning have a catalytic influence on oxidation (tyrosine); or its catalytic effect may appear in a later phase

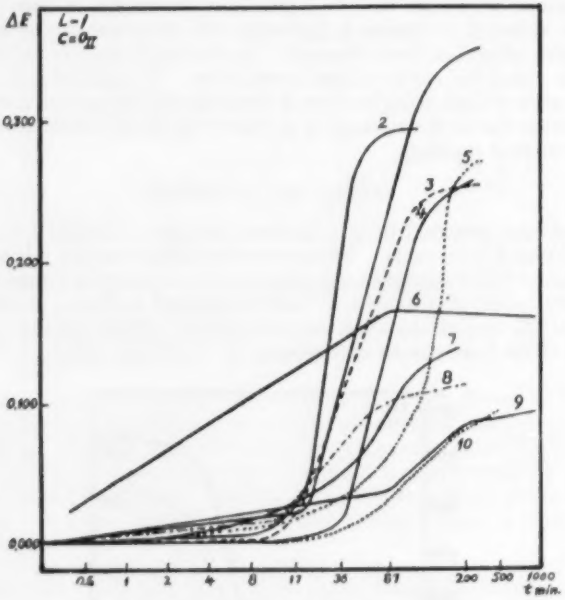


FIG. 17.—The abscissa represents the time in minutes.

1. 2% p-quinone.
2. 2% urea.
3. Pale crepe containing no agent.
4. 2% p-nitrophenol.
5. About 1% nickel diethyldithiocarbamate.
6. About 4% benzoyl peroxide.
7. 2% 1,2,4-dinitrophenol.
8. 2% phenyl-2-naphthylamine.
9. 2% benzidine.
10. About 4% pyrogallol.

(nickel diethyldithiocarbamate); or it may first accelerate and then inhibit oxidation (phenyl-2-naphthlamine); or it may act from the beginning as an antioxidant (pyrogallol). The fact that these substances even in very small quantities, can have such an influence on the course of the reaction proves that they take part directly in the chain reaction in all its phases. In order to control this reaction best it is necessary not to choose only a single type of antioxidant but to use a mixture of various antioxidants, so that all phases and all types of mechanisms of aging of natural rubber can be controlled. This can be carried out on the basis of an analysis of the corresponding experimental curves. It is necessary to keep this in mind in the study of industrial vulcanization where antioxidants are added during mastication before vulcanization. The effect of antioxidation mixtures during various types of aging, the effect of vulcanization agents, and the mechanism of vulcanization will be discussed in later studies.

In surveying the mechanism of action of antioxidants Field, Wood, and Gehman[4], and Semyonov[9] and others assume that an antioxidant acts in such a way that it transfers its own hydrogen to the isoprene radical while the reaction chain is ruptured and a stable free radical, itself hardly active, appears in order to begin the chain. Stevens[18] and other demonstrated the direct condensation of an antioxidant with rubber which exhausts the active reaction centers. Blake and Bruce[3], Bondy[19] and others[20] ascribe an essential role to the absorption of active light by the antioxidants. Krichhof[21] assumes that the protective effect, even in low concentrations of hydroquinone, consists in its reduction capacity.

Carpenter[22], on the basis of a study of the absorption of oxygen in rubber as related to pressure arrived at the conclusion that autocatalytic oxidation of rubber without any antioxidant is a chain reaction similar in principle to the oxidation of non-conjugated olefins. In the presence of antioxidants at constant oxygen pressure, a state of dynamic equilibrium of oxidation in its constant stage is reached. As we shall see in the discussion this observation agrees with our results.

The results of our measurements show that, although the influence of all the factors adduced is possible, the most important is the rate of formation of free radicals and their reactivity with another radical or a neutral molecule. According to this effect, we can often divide substances which influence aging into inhibitors, retarders, initiators, and catalysts of oxidation.

In certain substances, however, a combined effect is observed and it is, therefore, necessary to judge them according to their action at different stages of aging, e.g., as initiator-vulcanizers (benzoyl peroxide), etc.

From the experimental curves it is possible to distinguish the type of the corresponding substance. We follow this scheme:

I. The more active is the antioxidant (AH) molecule with the rubber radical (R·), the more the initial segment of the curves is prolonged:

$$AH + R\cdot \longrightarrow A\cdot + RH$$

Further effect depends on the reactivity of the new free radical (A·) of the antioxidant:

A. with the rubber molecule (RH)
B. with the rubber radical.

In case A in the type of reaction:

$$A\cdot + RH \longrightarrow R\cdot + AH$$

(a) if the radical (A·) is inactive the curve is very low in the stationary phase—*inhibitors*.

(b) if the radical is not very active, the curve has a low stationary segment.

(c) if the radical is very active, the curve has a high stationary segment—*retarders*.

In case B in the type of reaction:

$$A\cdot + R\cdot \longrightarrow A - R$$

the stationary part of the curve is lower (rapid consumption of antioxidant, type of side chain formation); *the most effective inhibitor*.

II. The more easily the molecules of the admixture (KH) form free radicals be decomposing (initiators), the shorter is the initial period of the reaction curves.

Reaction type:

$$KH + h\nu \longrightarrow K\cdot + H\cdot$$

The height of the curves at equilibrium in the stationary part depends on the concentration of catalyst. If the concentration is small, scheme I is valid. At higher concentrations, scheme III is valid.

III. A great number of new radicals R· increases the probability of side-chain formation ($R\cdot + R\cdot \longrightarrow R - R$). The reaction centers capable of oxidation are thereby quickly exhausted and the increase of C=O groups is less than in pure rubber.

If the catalyst radical K· is also reactive with the isoprene radical R· ($K\cdot + R\cdot \longrightarrow KR$), fewer oxidation centers are exhausted and the curve is higher than in the first case, although lower than in pure rubber.

The same course is observed for the curves when a large number of centers is formed as the result of intensive irradiation at low temperature[1].

The concentration of oxygen and the temperature which accelerates oxidation rather than side chain formation have an essential influence on the height of the curves[1]. The influence of the concentration of catalyst and the determination of the maximum value at which the rate of oxidation is maximal in comparison with the rate of vulcanization (lowest curves) will be discussed in future studies in connection with the study of the influence of intensity of light and temperature.

By studying the curves it is possible to determine the reactivity of various types of substances and their free radicals, not only in the oxidation of rubber, but also in other chain reactions such, as polymerization and aging of various other synthetic high polymers. On the basis of our results we have put together a condensed table where the individual compounds are arranged according to their influence on the light aging of rubber. All the measurements from which the table was compiled were made under the same experimental conditions with the same mercury tube. The measurement for tyrosine was made with another apparatus, and consequently it is not included in all the tables.

Table 1 shows the properties of antioxidants or initiators which were studied. A number of mixtures studied are listed in Table 2 according to the mean wave-length time. As we have seen the mean wave-length time is not sufficient to characterize the antioxidation effect, particularly when the experimental curves do not have the same form. In order to characterize an antioxidant, it is necessary to know the course of the entire curve in order to determine

TABLE 1

EFFECT OF SOME COMPOUNDS DURING THE LIGHT AGING OF RUBBER

(Mercury-quartz tube L-1; distance 18 cm.; temperature 28° C)

Compound	Appearance of 0.5% rubber solution after 4 hours' shaking	Color of sheet before and after exposure	Physical appearance of sheet after exposure	Initial period in minutes	Ascending course	Mean wave length time (in minutes)	$\Delta E/CO_{II}$ in stationary phase	Effect (2% substance by weight of rubber)
Crude rubber	thick sol	colorless	sticky, cracked	13–15	normal	45	245	—
Benzoyl peroxide	thick yellowish sol	colorless	smooth, glossy, not cracked	—	nearly linear, rising from beginning	3	162	initiator-vulcanizing agent
Tyrosine (L-2)	fluid sol	colorless	very sticky (37 min.)	25	rising steeply	60	560	(0.5%) catalyst
Quinone	fluid sol	colorless	cracked (90 min.)	19	normal	50	350	catalyst
Quinhydrone	sol	colorless	cracked later (140 min.)	56	normal	56	168	inhibitor
Hydroquinone	sol	colorless	not cracked	40	arched from beginning	106	135	—
Pyrogallol	liquid sol	colorless	not cracked, not sticky, glossy	50	arched	120	110	inhibitor
o-Nitrophenol	thick gel	colorless	badly cracked, sticky (90 min.)	11	rising rather steeply	46	336	catalyst
p-Nitrophenol	excellently fluid sol	colorless	slightly cracked later	34	normal	71	260	retarder
m-Nitrophenol	thick fluid sol	colorless	not cracked, brown, somewhat elastic	29	rising gently	91	120	inhibitor
1,2,4-Dinitrophenol	fluid sol	yellowish; brown	relatively elastic not sticky	10	arched	63	144	catalyst-vulcanizing agent-inhibitor
Aminophenol	good fluid sol	yellowish; bright yellow after 15 minutes	not cracked, not sticky, relatively elastic	20	normal	56	155	inhibitor
Urea	thick gel	colorless	cracked (185 min.)	13	rising rapidly	30	292	catalyst
Thiourea	thick sol	colorless; reddish brown after 3 minutes	cracked, smooth	20	rising rapidly	50	290	catalyst
Phenyl-2-naphthylamine	sol	colorless	reddish brown after 3 minutes	12	normal	30	120	catalyst-vulcanizing agent
Nickel diethyldithiocarbamate	good fluid sol	greenish; colorless	smooth (90 min.) cracked (210 min.)	20	large, arched	142	260	(1.5%) retarder
Benzidine	thick gel	colorless; yellow after 3 minutes	not cracked, not sticky (even after 2000 min.)	50	slow rise, after linear beginning	160	95	inhibitor-vulcanizing agent

TABLE 2

Number	Compound	Mean wave length time (in minutes)
1	Benzoyl peroxide	3
2	Urea	30
2	Phenyl-2-naphthylamine	30
3	Rubber	45
4	*o*-Nitrophenol	46
5	Quinone	50
5	Thiourea	50
6	*o*-Aminophenol	56
7	1,2,4-Dinitrophenol	63
8	Quinhydrone	66
9	*p*-Nitrophenol	71
10	*m*-Nitrophenol	91
11	Hydroquinone	106
12	Pyrogallol	120
13	Nickel diethyldithiocarbamate	142
14	Benzidine	160

the initial period, as well as the height of the stationary phase. The study of the relation between the course of the curve and the concentration of antioxidant provides additional important information. Individual substances are listed in Table 3 according to the length of the initial period in minutes and in Table 4 according to the height of the stationary segment of the curves. The tables will be complete after additional measurements of the molecular weights.

BRIEF SCHEME

Long initial period-low stationary phase.

The antioxidant molecule reacts readily with the rubber radical. Its own free radicals are not very active with the rubber molecules (inhibitor).

Long initial period-high stationary phase.

The antioxidant molecule reacts readily with the rubber radicals. Its own free radicals react readily with the rubber molecules (retarder).

Short initial period-low stationary phase.

TABLE 3

	No.	Compound	Initial period (in minutes)
Catalysts in induction period	1	Benzoyl peroxide	0
	2	1,2,4-Dinitrophenol	10
	3	*o*-Nitrophenol	11
	4	Phenyl-2-naphthylamine	12
	5	Urea	13
	6	Rubber	13–15
Prolonged induction period	7	Quinone	19
	8	Nickel diethyldithiocarbamate	20
	8	Thiourea	20
	8	*o*-Aminophenol	20
	9	*m*-Nitrophenol	29
	10	*p*-Nitrophenol	34
	11	Quinhydrone	36
	12	Hydroquinone	40
	13	Pyrogallol	50
	13	Benzidine	50

TABLE 4

Number	Compound	$\Delta E/CO_{II}$ in stationary phase	
1	Quinone	350	upper
2	*o*-Nitrophenol	336	stationary
3	Urea	292	segment
4	Thiourea	290	
5	*p*-Nitrophenol	260	
5	Nickel diethyldithiocarbamate	260	
6	Rubber	245	
7	Quinhydrone	168	lower
8	Benzoyl peroxide	162	stationary
9	*o*-Aminophenol	155	segment
10	1,2,4-Dinitrophenol	144	
11	Hydroquinone	135	
12	Phenyl-2-naphthylamine	120	
12	*m*-Nitrophenol	120	
13	Pyrogallol	110	
14	Benzidine	95	

The molecule readily forms its own free radicals which react with the rubber molecule or radical. Owing to the large concentration of R· radicals, side-chain formation takes place in the later stage (initiator-vulcanizer).

Short initial period-high stationary phase.

The molecule readily forms free radicals, but the value of the maximum concentration is not exceeded (initiators).

SUMMARY

A method was worked out for the determination of the effect of antioxidants and other substances on the course of the light-aging of rubber. The experimental curves of the relation between the increase of C=O groups and the exposure time, determined by infrared spectra were used as criteria. The action of the following substances was studied: benzoyl peroxide, phenyl-2-naphthylamine, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, 1,2,4-dinitrophenol, *o*-aminophenol, quinone, quinhydrone, hydroquinone, pyrogallol, nickel diethyldithiocarbamate, benzidine, urea, thiourea, and tyrosine. These substances can be divided into inhibitors, retarders, and initiators of oxidation according to their action. Study of the influence of variation of the concentration of antioxidant showed that a definite optimal concentration exists, beyond which the effect is greatly weakened. It was likewise shown that in order to determine the antioxidation effect, it is necessary to know the entire course of the experimental curve in all phases of aging. It was further shown that the addition of a mixture of benzoyl peroxide (oxidation initiator) and pryogallol (antioxidant) results in an effect which depends on the proportions of both ingredients, so that the vulcanizing action of the peroxide, as well as the antioxidation action of pyrogallol are approximately additive; that is, according to the proportions present. From a study of substances such as *p*-quinone, quinhydrone, hydroquinone, and pyrogallol, it appears that the antioxidation effect is closely connected with the oxidation-reduction potential of the rubber-oxygen-antioxidant system.

The antioxidation effect of *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol was compared, and no relation was found between the action of the derivative

and its dipolar moment. In studying the relation between the rate of reaction and the structure of the ingredient, it is necessary to take into consideration the theory of mean induced polarity. Replacement of the nitro group by the amino group (comparison of *o*-nitrophenol with *o*-aminophenol) causes the phenol derivative of benzene to become an effective antioxidant. It was established that phenyl-2-naphthylamine is not an effective antioxidant in the initial phase of light aging, but is effective in the later phase.

The study of the effect of tyrosine as an ingredient of the natural proteins of crude rubber showed that natural oxidation catalysts are present in crude rubber, besides natural antioxidants, and this natural oxidation-reduction system determines the properties of crude rubber. Since this system can be very diverse, both qualitatively and quantitatively, it is possible to explain the great variation in the quality of natural rubber of even the same type. In conclusion, it can be stated that, in order to control the chain mechanism of aging of natural rubber, it is necessary to choose a mixture of different antioxidants and oxidation initiators, in order to control all phases and types of aging reactions. This can be done on the basis of the corresponding experimental curves. Their study makes it possible to follow the reactivity of various types of substances and their free radicals, not only during the oxidation of rubber, but also during other reactions with chain mechanism, such as polymerization and aging of various other synthetic high polymers and natural substances.

The results of measurements show, further, that antioxidants take part directly in the reaction, and that the most important factor in the antioxidation action is the rate of formation of free radicals and their reactivity with other radicals, as well as with neutral molecules. On the basis of these results, summary tables are compiled, in which the individual compounds are listed according to their influence on the course of rubber aging.

Finally a scheme of the reaction mechanism is given for the four fundamental types of experimental curves: namely, those with long initial and low stationary segments, long initial and high stationary segments, short initial and low stationary segments, and short initial and high stationary segments.

REFERENCES

[1] Tkáč and Kellö, *Chem. Zvesti* **7**, 257 (1953).
[2] Kellö and Tkáč, *Chem. Zvesti* **7**, 129 (1953).
[3] Blake and Bruce, *Ind. Eng. Chem.* **33**, 1198 (1941); Rubber Chem. & Technol. **12**, 181 (1939).
[4] Field, Woodford and Gehman, "Symposium on High-Polymer Physics", edited by Robinson, New York, **1949**, p. 28.
[5] D'Or and Kössler, 3e Congrès National des Sciences, Brussels, **1950**.
[6] Stevens, *J. Soc. Chem. Ind.* **35**, 872 (1916).
[7] Billmann and Lund, *Ann. chim. phys.* **16**, 321 (1921); Billmann, *Ann. chim. phys.* **15**, 109 (1921); *Trans. Faraday Soc.* **19**, 57 (1923); Billmann and Krarup, *J. Chem. Soc.* **125**, 1954 (1924).
[8] Bolland and Ten Have, *Discussions Faraday Soc.* **2**, 252 (1947).
[9] Semyonov, *Uspekhi Khim.* **20**, 673 (1951).
[10] Bagdasaryan, *Zhur. Fiz. chim.* **23**, 790 (1949).
[11] Williams and Krehma, *J. Am. Chem. Soc.* **49**, 1878 (1927).
[12] Hückel, "The Dipole Moment and the Velocity of Reaction", in Debye, "The Dipole Moment and Chemical Structure", London, **1931**, p. 79.
[13] Meerwein, *Ber.* **53**, 1815 (1920); **55**, 2500 (1922); *Ann. Chem.* **435**, 207 (1924).
[14] Hückel, "The Dipole Moment and the Velocity of the Reaction", in Debye "The Dipole Moment and Chemical Structure", London, **1931**, p. 88.
[15] Vorländer, *Ber.* **37**, 1646 (1904); **52**, 263 (1919); Allan, Oxford, Robinson, and Smith, *J. Chem. Soc.* **1926**, page 404; Hückel, "The Dipole Moment and the Velocity of Reaction", in Debye, "The Dipole Moment and the Chemical Structure", London, **1931**, p. 88.
[16] Pinassi, *Rev. gén. caoutchouc*, **28**, 567 (1951).
[17] Tristram, *Biochem. J.* **34**, 301 (1940).
[18] Stevens, "Rubber Photogels and Photovulcanizates", in Kraemer, "Scientific Progress in the Field of Rubber and Synthetic Elastomers", New York, **1916**, p. 387.
[19] Bondy, *Rev. gén. caoutchouc* **11**, 1, 6, 9 (1934).
[20] Kirchhof, *Gummi-Ztg.* **44**, 252 (1929); Spence and Ferry, *J. Am. Chem. Soc.* **59**, 1648 (1937).
[21] Kirchhof, *Kautschuk* **9**, 70 (1933).
[22] Carpenter, *Ind. Eng. Chem.* **37**, 187 (1947).

STUDY OF THE REACTION KINETICS OF AGING OF NATURAL RUBBER BY INFRARED SPECTROGRAPHY IV. INFLUENCE OF WAVE LENGTH OF LIGHT AND TEMPERATURE ON LIGHT AGING *

A. Tkáč, V. Kellö, and J. Hrivíková

Chair of Physical Chemistry of Slovak Technical High School, in Collaboration with the Research Institute of Cables and Insulators in Bratislava, Czechoslovakia

As we remarked in a preceding article[1], the course of the light aging of natural rubber depends to a large degree on the wave length and intensity of the light source, as well as on the experimental temperature. These factors have been studied only qualitatively until now. Because of their fundamental importance, we have studied the relation between these factors, as well as their relation to the aging of rubber, and, whenever possible, by means of infrared spectrography[2].

All the measurements published in the preceding works[3] were made with mercury tubes with quartz jackets. These will be designated by L-1, L-2, L-3, etc. The separate sources of radiation are thus distinguished because the form of the curves of the reaction kinetics of rubber aging depends considerably on the composition of the spectrum of the source, which can vary in different apparatus. A definitive comparison of the curves is possible only when the source is precisely defined.

In general, we have used high-pressure PHILORA mercury tubes, types HP-300, HP-500 (usually with no outer jacket), as well as a high-pressure ultraviolet tube HPW-125W. We present the spectrum characteristics of these lamps, as given by Oranje[4], in Figures 1 and 2. These lamps were fed from a stabilizer VILNES 250 VA (stability $\pm$ 0.5%).

The curves of reaction kinetics are depicted in Figures 3 and 4 in the form of the relation between the increase of C=O groups and the logarithm of the time of exposure in unextracted and extracted rubber. If the tube has no glass jacket, which holds back most of the ultraviolet component of the radiation, the course of oxidation is represented by the curve *a*. If the ultraviolet component is cut off by the jacket, the induction period is consideraly prolonged (from 30 to 400 minutes in unextracted rubber and from 15 to 200 minutes in extracted rubber; curve *b*). If a lamp of equal wattage is used, in which all the spectral bands except the ultraviolet (3655 Å) are filtered out, the induction period is still longer (1600 minutes in unextracted rubber and 800 minutes in extracted rubber; curve *c*). This shift is not due to the fact that the corresponding ultraviolet band is less active, but rather that the other active bands are lacking in the radiation. Figures 5 and 6 show the activity of the separate bands of the spectrum of a mercury tube; they represent the curves of oxidation at various wave lengths of effective radiation. Monochromatic radiation was studied by

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Chemicke Zvesti*, Vol. 8, No. 1, pages 3-13, January 1954

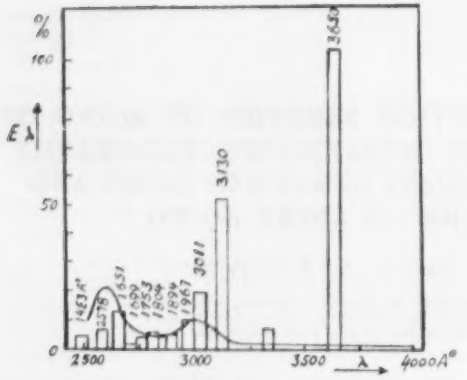


FIG. 1.

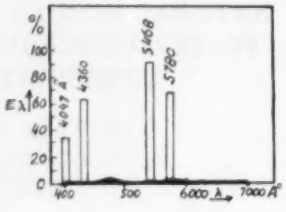


FIG. 2.

absorption filters (Zeiss), which admit only one band of the spectrum of the mercury tube. Since, however, the relative intensities of these bands were different, the measurements had to be adjusted to make possible a comparison of the effectiveness of the individual wave lengths at the most uniform possible intensities of radiation I. This can be obtained approximately by adjusting the distance between the source and the exposed surface: $r \left(I = \frac{E}{r^2} \cos \alpha \right)$. The relative values of spectral radiation E of the individual bands of the spectrum of high-pressure mercury tubes are shown in Figures 1 and 2. We used West's data[5] for a comparison of the radiation of the 5460 Å band and the 3650 Å ultraviolet band.

Table 1 presents the data for the calculation of the distances used, on the assumption that the light fell perpendicularly on the surface of the sheet (cos $\alpha = 1$).

Figures 5 and 6 show clearly that, in the visible range of the spectrum, bands 5780 Å are inactive. However, band 4360 Å is active, while the activity of 4050 Å is slight. The ultraviolet band 3650 Å is again very active, and the curve practically agrees with the curves *c* in graphs 3 and 4, obtained by a mono-

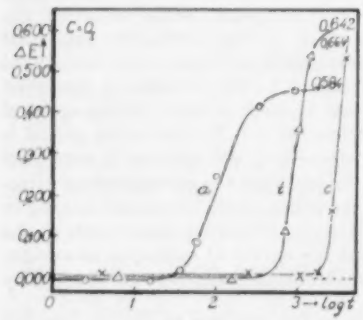


FIG. 3.

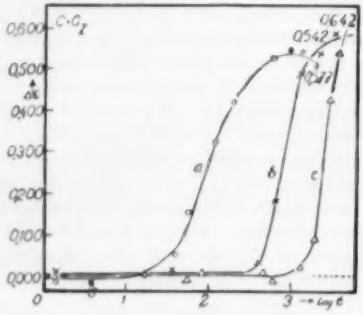


FIG. 4.

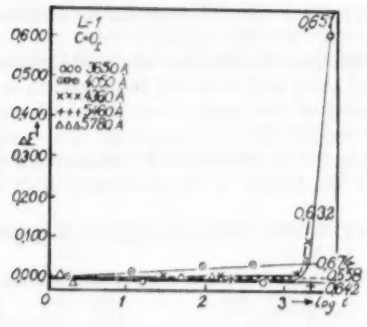


FIG. 5.

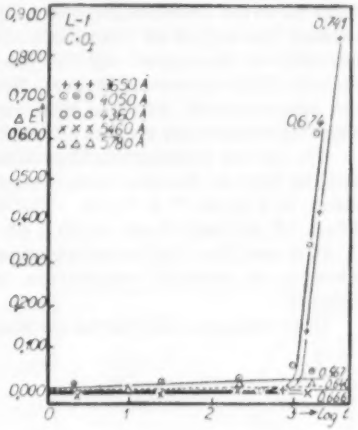


FIG. 6.

chromatic lamp HPW-125 W. These results agree with the data of those authors[6] who declare the upper limit of effectiveness of radiation on oxidation of rubber to be in the range of 4400 Å. All the results of previous studies of the effectiveness of individual spectral bands on the oxidation of rubber were obtained by different methods. The close agreement between their conclusions and our results shows that the study of the increase of C=O groups leads to the same results as other methods based on the study of the average properties of the entire specimen.

The induction periods in extracted rubber compared with unextracted rubber were about 50 per cent shorter at all wave lengths (Figures 3, 4, 5, 6). Since the extraction was thorough (mixture of acetone-methanol 1:1 for more than 3 months), it is possible to assume that only a minimal quantity of natural antioxidants is present in the specimen. This proves that the induction period is not governed by the exhaustion of natural antioxidants, but is the result of a chain mechanism, most probably with degenerated chain formation. Since the effect of eliminating the natural antioxidants is practically the same at all the wave lengths studied, it is impossible to assume that the protective effect of the natural antioxidants is based on selective absorption of effective radiation.

We also studied the influence of the intensity of radiation on the course of the oxidation of rubber at constant temperature. We used a thermostatic device previously described[1], in which the temperature was kept within an accuracy of ±0.5° C. The mercury tube HP-300 was chosen as source. In

TABLE 1

Band λÅ	Relative intensity E'	Transmission of filter T (%)	Intensity of admitted light $E(E=E'\cdot T)$	Calculated distance r(for $I=1$)	Distance used d in cm. ($=2r$)
5780	60	71.0	42.5	6.51	13.0
5460	88	76.0	66.8	8.16	16.3
4360	64	31.0	19.8	4.45	8.9
4050	34	70.0	23.8	4.87	9.7
3650	100	29.5	29.5	5.42	10.8

order to avoid over-heating the specimen, particularly at short distances, we reduced the output of the tube to 35 W. As a result of the lowering of the intensity of the source and the modified spectral composition the induction periods of the curves are longer. Since the source was precisely defined in all the measurements, however, the comparison of the different curves and the resulting conclusions are not affected.

The curves representing the relation between the increase of $C{=}O_I$ groups and the time at various intensities of radiation and constant temperature are shown in Figures 7, 8, 9, 10. The distance of the source from the sheet was 2.5, 5, 10, 15, and 25 cm. at 16.5, 35, 62 and 80° C.

It is seen that the induction period is generally shortened by an increase of intensity at constant temperature, while the height of the stationary part is reduced.

If we compare the curves obtained at various temperatures and constant

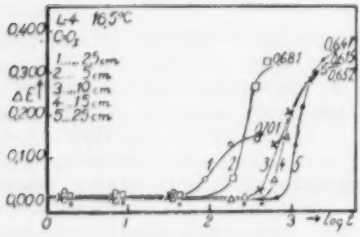


Fig. 7.

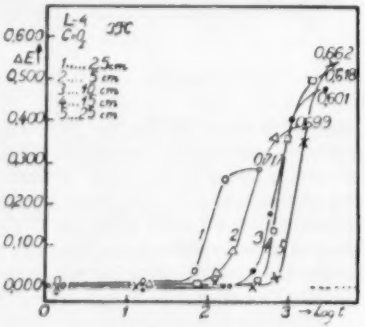


Fig. 8.

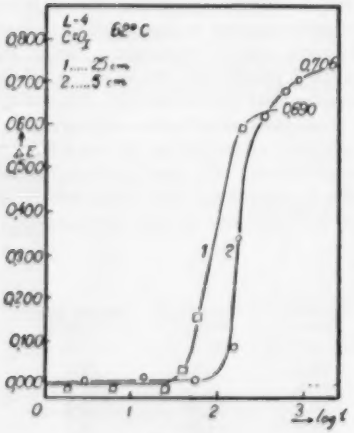


Fig. 9.

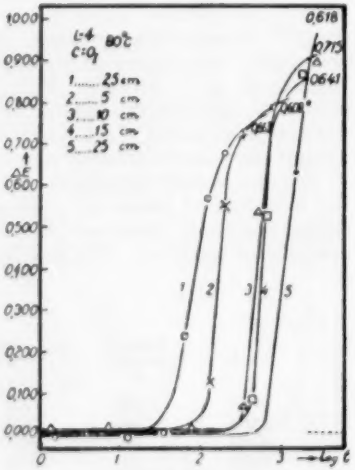


Fig. 10.

intensity (Figures 11, 12, 13, 14, 15), we see that an increase in temperature shortens the induction period and raises the stationary part.

Quantitative study of the induction periods in the form of the relation between their length and the intensity of radiation (indirectly proportional to the square of the distance) leads to the curves shown in Figure 16.

As a more detailed analysis shows, these curves can be expressed in the range of temperatures and intensities studied by the relation:

$$I \cdot t^a = K$$

where I is the reciprocal of the square of the distance ($I = 1/r^2$), proportionla to the intensity of radiation, t is the length of the induction period, and a and K

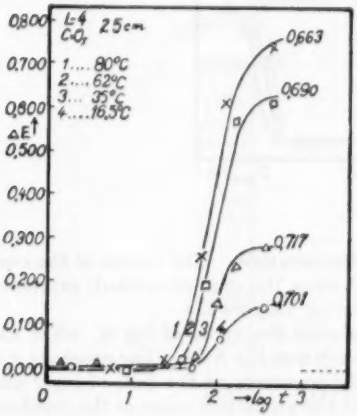


Fig. 11.

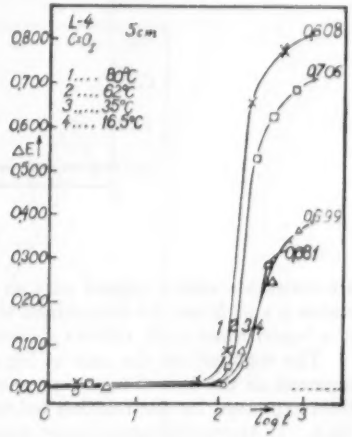


Fig. 12.

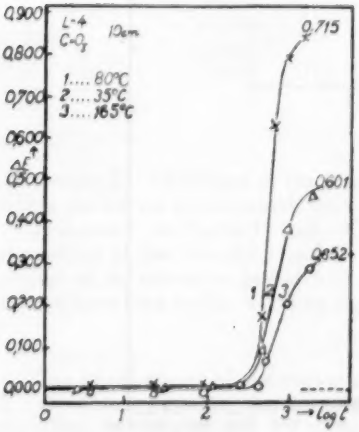


Fig. 13.

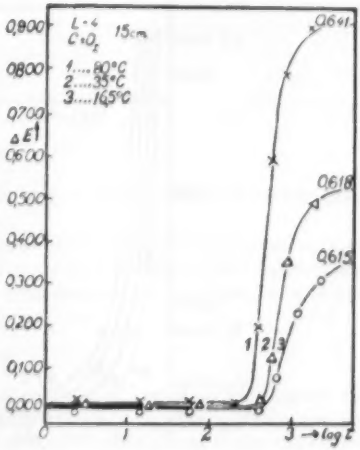


Fig. 14.

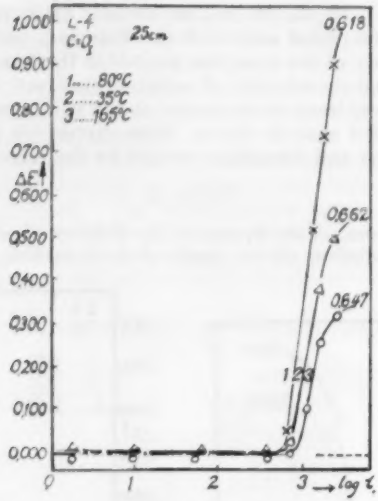


FIG. 15.

are constants which depend only on the temperature. The values of the constants a and K can be determined simply, since the relation quoted, expressed in a logarithmic scale, follows a linear relation (Figure 17).

The segment on the axis of $\log I$ expresses the value of $\log K$, while the segment on the axis of $\log t$ expresses the relation $\log K/a$. The constant a is then expressed by the relation between the segments on the axes of $\log I$ and $\log t$. In the temperature range measured the numerical value of the constant

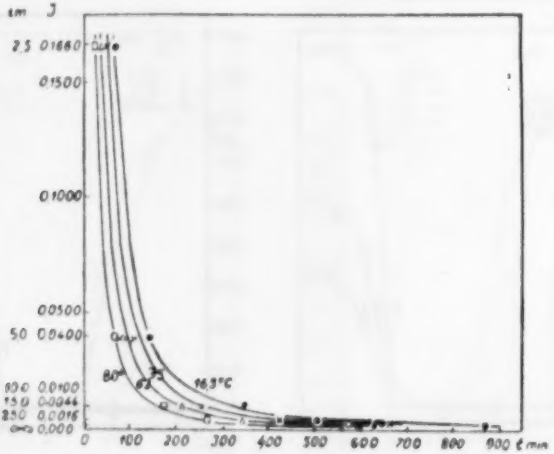


FIG. 16.

a lies between 1.5 (at 80° C) and 1.8 (at 16.5° C). The value of K decreases rapidly with the temperature; for example, it falls from 300 at 16.5° to 20 at 80° C (if the distance of the source is given in cm. and the time in minutes). The value of K falls with the higher value of the absolute temperature, which is closely connected with the great sensitivity of the rate of the chain reaction to variations in temperature. Approximate calculation shows that, at about 230° C, the values of K and a are equal to unity and the curve of the dependence of the induction period on the intensity of radiation would form a hyperbola very near the coordinates. It appears from a comparison of the curves in Figure 16 with the results obtained in the study of heat aging in darkness[7], that the length of the induction period during heat aging can be estimated on the assumption that aging in darkness is characterized by a very low value of the

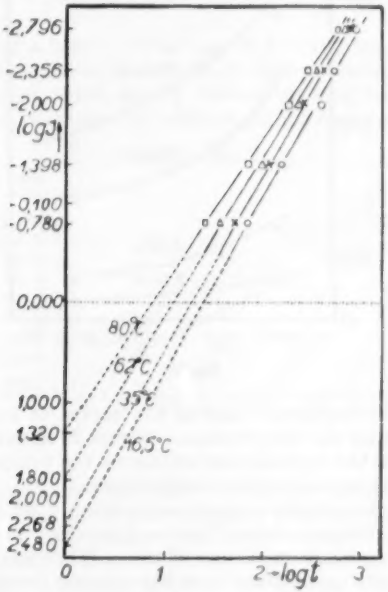


FIG. 17.

coordinate I. The length of the induction period is thus indicated by the place where the curves almost touch the t-axis.

It is seen from Figure 18 that an increase of the temperature causes a rapid shortening of the induction period. Neiman and collaborators[8] derived the change of the induction period with the temperature for pentane, butane and butene according to the following equation:

$$t \cdot e^{\gamma/T} = C$$

The linear course of the curves of the relation of $\log t$ to $T/1$ (Figure 19; T—absolute temperature) demonstrates the validity of this relation for the oxidation of rubber as well. The values of the constant γ and C depend on the intensity of radiation.

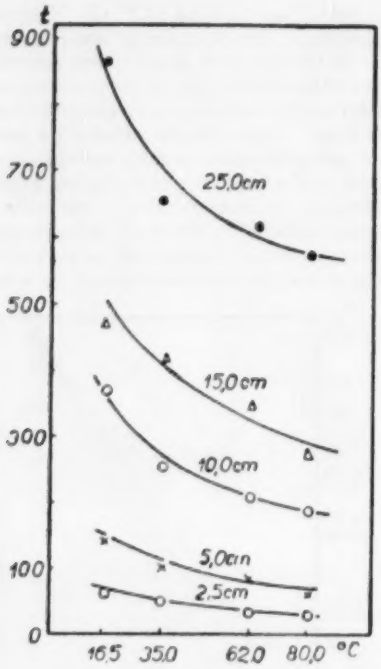


FIG. 18.

The height of the stationary part of the curves at constant intensity of radiation increases with the temperature. Figure 20 shows the linear dependency of the height of the experimental curves on the temperature. The individual lines represent various radiation intensities.

It is thus seen that heat aids oxidation considerably, while a higher intensity suppresses it. The different action of heat and intensity on oxidation is evident from a quantitative comparison of their effects. While an increase of temperature of about 60° C during exposure from 25 cm. raises the stationary part, that is, oxidation, about three-fold; a hundred-fold increase of intensity at 80°, on the other hand, lowers the stationary part of the curves by about one-third.

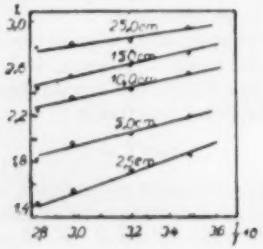


FIG. 19.

This is a fundamental addition to our qualitative conclusions, which were stated in preceding articles[3]. The more intensive is the radiation, the more free polyisoprene radicals (R·) are formed. In the presence of oxygen, the correlation between the rate of oxidation V_0 ($R\cdot + O_2 \rightarrow ROO\cdot$) and the termination of the chains V_s by the mutual recombination of free radicals ($R\cdot + R\cdot \rightarrow R - R$) depends on the number of primary radicals which appear. From the equations presented it is seen that, while the rate V_0 of appearance of oxidized radicals ROO· is, at constant oxygen concentration, proportional to the instantaneous quantity of new radicals R·, the rate of their recombination, that is, side-chain formation, V_s, is proportional to the square of the primary radicals:

$$V_0 = \frac{d[ROO\cdot]}{dt} = k_1[R\cdot]\cdot[O_2] \quad \text{and} \quad V_s = \frac{d[R{-}R]}{dt} = k_2[R\cdot]^2$$

In the presence of a large number of new free radicals, that is, at a high radiation intensity, the side-chain formation exhausts a large number of centers susceptible to oxidation, which greatly reduces the height of the experimental curves of the relation of increase of oxidized groups to time. Thus both proc-

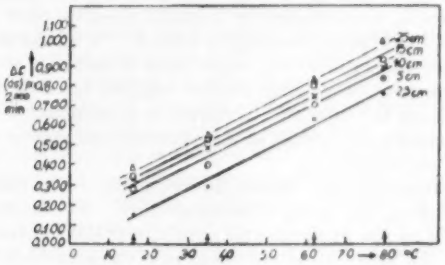


FIG. 20.

esses always take place simultaneously during the aging of rubber; that is, oxidation, leading to rupture of the polymers, and side-chain formation (vulcanization), leading to an increase of molecular weight[9]. It is true that, besides these most pronounced reactions, other reactions such as depolymerization, cyclization, and formation of ether side-bridges also take place. The relation between the rates of these reactions depends on the selection of aging conditions. For example, optimum conditions for vulcanization, with a simultaneous suppression of oxidation, are given by a low temperature and high intensity of radiation. Naturally, the reaction mechanism is greatly influenced by the addition of antioxidants, initiators, and retarders as described in the preceding article.[10]

The concept of simultaneous occurrence of destruction, as well as formation of polymers, is a natural result of the nature of the mechanism of chain reactions itself. While oxidation reactions can be regarded as the development of chains, vulcanization reactions are termination reactions. Since the heights of our experimental curves are determined by the relation between oxidation and vulcanization, it is possible to regard them as a measure of the length of the chains.

The influence of heat on the course of the reactions consists in the fact that, at a higher temperature, the liberation of energy caused by termination is

decreased. Thus, if the temperature is reduced, the liberation of energy by the surface of the specimen is more intensive, which makes possible the reaction: $R\cdot + R\cdot + X \rightarrow R - R + X^*$ (X is the molecule which receives the liberated energy). Thus the chains are shortened and the balance is shifted in favor of vulcanization.

Our conclusions about the simultaneous processes of vulcanization and oxidation agree with the hypotheses of some authors who have studied the aging of various synthetic and natural rubbers by other methods. In this connection one might cite the works of Cole and Field[11], Houwink[12], Dufraisse[13], Stevens[14], and Blake[15].

With a suitable selection of radiation intensity and composition (the most active bands of the solar spectrum) and experimental temperature, it is possible to make artificial tests of light aging in the laboratory which correspond sufficiently well to natural tests. It is evidently necessary to compare the natural and artificial tests under various weather conditions and at various seasons.

SUMMARY

The influence of the wave length of radiation on the process of photocatalytic aging of rubber, as well as the relations between the intensity of radiation and the temperature, were studied by infrared spectroscopy. The upper limit of effectiveness of light lies in the range of 4360 Å. While an increase of temperature greatly accelerates oxidation, an increase of radiation intensity retards it. Numerous analyses reveal an exponential relation between the length of the induction period and the intensity of radiation at constant temperature, and a linear relation between the height of the experimental curves and the temperature at constant intensity.

Oxidation destruction and side-chain formation (vulcanization) take place simultaneously during the aging of natural ruber. The relation between these reactions depends on the experimental conditions; the temperature accelerates oxidation, while the intensity of radiation aids vulcanization.

REFERENCES

[1] Tkáč and Kellö, *Chem. Zvesti* **7**, 257 (1953).
[2] Kellö and Tkáč, *Chem. Zvesti* **7**, 129 (1953).
[3] Tkáč and Kellö, *Chem. Zvesti* **7**, 257 (1953); Kellö and Tkáč, *Chem. Zvesti* **7**, 385 (1953); Kellö and Tkáč, *Chem. Zvesti* **7**, 385 (1953).
[4] Oranje, "Les Lampes a Décharge Philips".
[5] West, "Spectroscopy and Spectrophotometry", in Weissberger, "Physical Methods of Organic Chemistry", New York, **1949**, p. 1281.
[6] Yamazaki, *J. Soc. Chem. Ind. Japan* **30**, 804 (1927); Yamazaki, *J. Soc. Chem. Ind. Japan* **31**, 233, 243 (1928); Yamasaki and Okuyami, *J. Soc. Chem. Ind. Japan* **32**, 367B (1929); Yamazaki and Okuyama, *Caoutchouc et gutta-percha* **27**, 15, 16 (1930); Bondy, *Rev. gén. caoutchouc* **11**, 1, 6, 9 (1934).
[7] D'Or and Kössler, Extrait du III^e Congrès National des Sciences Bruxelles, May 30-June 3, 1950; and unpublished data.
[8] Neiman and Tutakin, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1**, 329 (1938); Avyazov, Neiman, and Chanova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1**, 307 (1938); Avramenko and Neiman, *Acta Physicochim. URSS* **10**, 60 (1939); Dobrinskaya and Neiman, in Nalbandan and Emanuel, "Kinetika Cepnyek Reakcií Okislenií", Moscow-Leningrad, **1950**, p. 164.
[9] Dogadkin and Sobeleva, *Zhurn. Fiz. Khim.* **25**, 72 (1952).
[10] Kellö and Tkáč, *Chem. Zvesti* **7**, 385 (1953).
[11] Cole and Field, *Ind. Eng. Chem.* **39**, 765 (1942).
[12] Houwink, *Kautschuk* **17**, 77 (1941).
[13] Dufraisse, in the "Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**.
[14] Stevens, "Rubber Photogels and Photovulcanizates" in Kraemer, "Scientific Progress in the Field of Rubber and Synthetic Elastomers", New York, **1946**.
[15] Blake, "The Effects of Light and Ozone on Rubber", Symposium on Aging of Rubbers", New York, **1951**.

X-RAY DETERMINATION OF CRYSTALLINITY IN DEFORMED RUBBER *

S. C. NYBURG

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

INTRODUCTION

Two previous x-ray determinations of crystallinity in simply extended natural rubber, those of Field[1] and of Goppel[2], showed considerable differences in magnitude. A redetermination, with an extension to other types of strain, has been carried out, using a rubber vulcanized with di-*tert.*-butyl peroxide. This is a more suitable material for two reasons than the conventional sulfur vulcanizates measured by the earlier investigators. First, peroxide vulcanization, which is thought to entail molecular chain cross-linking by polyisoprenic carbon atoms themselves, obviates the introduction of foreign material into the rubber and, second, the volume change caused by crystallization, which is obscured in sulfur vulcanizates by vacuole formation, but appears genuine in peroxide rubbers, has already been measured in these laboratories by Stern[3].

The theory underlying the determinations is that, since the total x-ray intensity from a given specimen is independent of the arrangement of the constituent atoms[4], there will be a compensating diminution of integrated amorphous intensity when an initially amorphous material is caused to show crystalline-type scatter by deformation or in some other way. The degree of crystallinity is then defined as the fractional decrease of integrated amorphous intensity, but this ignores any crystalline regions so small or so disordered that they would give rise to scatter inseparable from the amorphous scatter. Accordingly, it does not necessarily follow that crystallinity determined by X-rays will be the same as that given by other methods which will be differently sensitive to that crystallinity which escapes x-ray measurement.

The amorphous intensity *distribution* round the x-ray beam has been found, by other investigators and in the present work, to be independent of deformation. Accordingly, it is sufficient to measure, say, the diminution in *peak* intensity of the most intense halo at $(\sin\theta)/\lambda = 0.10$.

If I_u is the amorphous halo peak intensity of an undeformed completely amorphous specimen and, other things being equal, I_d the corresponding intensity in the deformed state, the percentage crystallinity is $100(I_u - I_d)/I_u$.

MATERIAL AND APPARATUS

Crepe rubber was lightly milled with the vulcanizing reagent and pressed into smooth sheets 2.5 mm. thick. It was extracted with hot acetone for two days after vulcanization, dried in a vacuum, and stored in the dark in a vacuum. It had a molecular weight between cross-links, estimated by equilibrium swelling

* Reprinted from the *British Journal of Applied Physics*, Vol. 5, No. 9, pages 321–324, September 1954.
The present address of the author is the Department of Chemistry, University College of North Staffordshire, England.

in benzene[5], of 7100 and an analysis corresponding to 96 per cent rubber hydrocarbon.

The camera, shown in Figure 1(*a*), was a modified version of the single-crystal goniometer[6]. The collimator was mounted more rigidly than in the standard design and was not moved between exposures. Inside the 3 cm. radius film holder, and coaxial with it, was a perspex tube 5 mm. thick, to the bottom of which was fitted a slotted steel ring which could be firmly located on the goniometer base. An equatorial zone of the tube was cut away apart from four uprights, one of which, central in the beam, held a powder pellet for exposure standardization, as in Goppel's measurements. Although the investigation was confined to exposures made at room temperature, the inside and outside of the tube were covered with 0.25 mm. celluloid sheet to provide insulation should exposures at other temperatures be required. The powder pellet was held in a brass bush and fitted with a thin steel conical screen as shown in

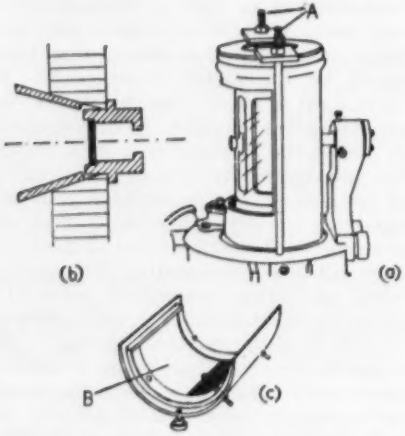


FIG. 1.—(*a*) X-Ray camera; (*b*) Powder assembly; (*c*) Film holder.

Figure 1(*b*). The whole assembly was rigidly held to the body of the goniometer by an upper circular brass plate, bolted to uprights *A*. A semicylindrical section, 8.3 cm. high, was cut from the original film holder and a new, flanged holder made to fit [Figure 1(*c*)].

The radiation used was nickel-filtered copper at 45 kV from a CA-6 type sealed-off self-rectified tube. Half the film was screened with 0.31 mm. aluminum sheet *B*; the difference of intensity on the two halves of the film simulates monchromatic values. Owing to increasing white radiation with target use, the somewhat imperfect monochromatization caused a small drift in calibration during sixty hours' total exposure. Allowance for incoherent scatter was made from the data of Simard and Warren[7].

The powder line used for standardization was the 4.3 Å reflection from a pellet of calcium sulfate dihydrate 0.3 mm. thick, diluted with a four-fold volume of graphite so that it could easily be made of uniform thickness.

Once deformed as described below, the appropriate region of the rubber was compressed between steel rectangles having the channelled-out cross-section

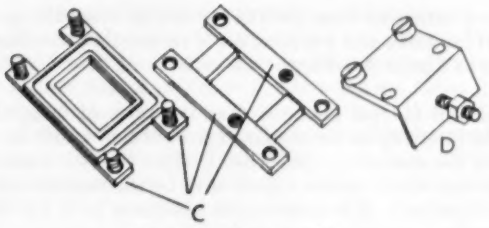


FIG. 2.—Specimen assembly.

shown in Figure 2. Over these rectangles were placed slotted steel strips C having threaded holes at the ends. Once in place, pressure was applied by a G-clamp, which left the holes at the ends of the strips clear. The excess rubber was trimmed away, the two rectangular clamps were tightly screwed together and the G-clamp removed. The assembly was then screwed to the support D, which in turn was screwed firmly into the central stem of the goniometer.

The films[8] were photometered with a non-recording photometer[9]. The two types of deformation examined had principal extension ratios α_1 vertical and the plane of the sheet normal to the beam. On the resulting photographs the amorphous halo can be photometered along a radial line inclined at 15° to the equator.

PRELIMINARY PROCEDURE

Photographs were corrected for air scatter by taking a number of exposures without rubber specimens and photometering at $(\sin\theta)/\lambda = 0.1$. The correction was assumed to hold when the rubber specimens were in place.

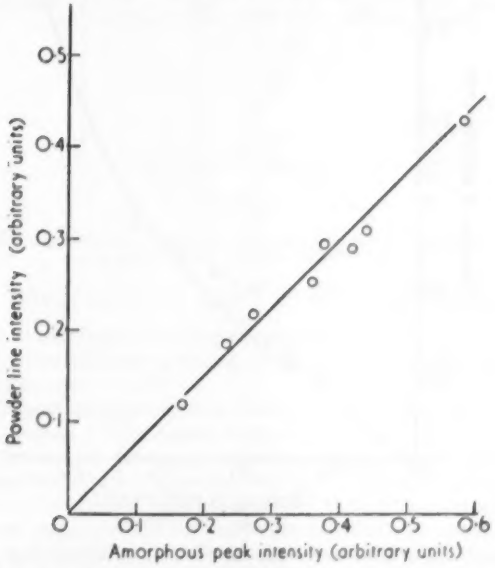


FIG. 3.—Initial calibration.

The ratio of intensity from the rubber to that from the powder should be independent of intensity and a typical set of results for a specimen about 1 mm. thick is shown in Figure 3. Three such ratios were determined for each specimen.

Both Field and Goppel assumed that the ratio of integrated amorphous intensity to the intensity of the standard powder line would be proportional to the thickness of the specimen. It is easy to show that for a sheet normal to the incident beam this would not be expected to be the case except for very small thicknesses. Moreover, it is safer not to assume a form for the ratio, but to measure it directly.

Very thin sheets of undeformed rubber, the thickness of which is difficult to measure accurately, were not used for this calibration, since deformed specimens, which are sufficiently hard and uniform to give reliable thickness measurements with a gauge, give intensity ratios which converge on the calibration line as deformation is decreased. This, together with the nonlinearity of the calibration, is seen in Figure 4.

CRYSTALLINITY INDUCED BY SIMPLE EXTENSION

Simple extension is attained by stretching narrow strips to a principal extension ratio $\alpha_1 = \alpha$; the other extension ratios are then $\alpha_2 = \alpha_3 \simeq \alpha^{-\frac{1}{2}}$. Volume changes are only about 2 per cent at $\alpha_1 = 5.0$ so that the thickness, which must in any case be known, can be used for estimating α_1.

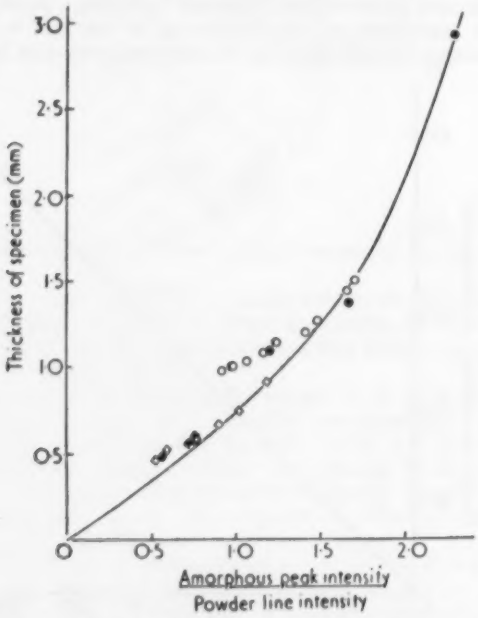


FIG. 4.—Intensity ratios as a function of specimen thickness. ⊕ = undeformed; ○ = simple extension, unheated; ● = simple extension, heat treated; ◇ = pure shear, unheated; ◆ = pure shear, heat-treated.

The strips, of measured initial thickness, were stretched by screw-operated clamps to the desired value of α_1 and then fixed vertically at the center of the rectangles described above. The stretching was normally completed in five minutes. The results, shown in Figure 5, curve (*a*) are taken from the values in Figure 4.

It is known that the degree of crystallinity of rubber depends, not only on the strain, but on the route by which the strain is attained. If highly extended specimens are partially relaxed, they show hysteresis effects which can be removed by heating. The result of heat treatment is, therefore, a guide to the closeness of the specimen to its equilibrium crystallinity. Two specimens in simple extension were heated at 90° C in a vacuum for one hour and allowed to cool for twenty-four hours at room temperature. The results for these are also shown on Figure 4, the small changes in crystallinity caused by this treatment being in accord with Goppel and Arlman's observations[10].

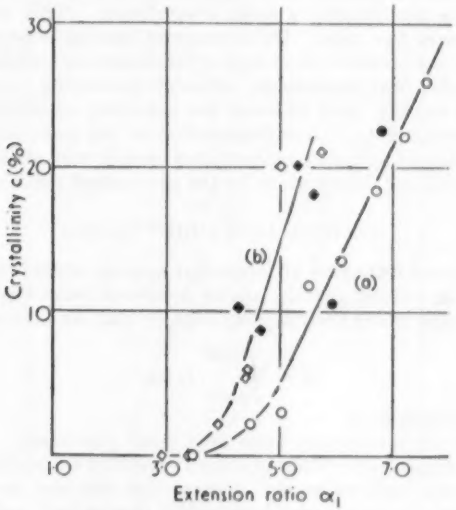


FIG. 5.—Dependence of crystallinity on extension for curve *a*, simple extension; curve *b*, pure shear. Key is same as for Figure 4.

CRYSTALLINITY INDUCED BY PURE SHEAR

Pure shear is attained when the extension ratios are $\alpha_1 = \alpha$, $\alpha_2 = 1.0$ and $\alpha_3 \simeq \alpha^{-1}$. The crystalline type scatter is different from that in simple extension because of higher orientation[11].

The undeformed specimens were sheets 65 × 15 mm., the principal stress being applied normal to the longer edge. In addition to the screw-operated clamps used for simple extension, screw-operated clamps mounted at right angles were used to obtain a sideways extension ratio α_2 of unity.

Two deformation routes were studied: (1) that with sideways extension α_2 kept constant at unity throughout the entire deformation (constant α_2 method) and (2) that with no sideways stress applied until the principal extension α_1 had reached the required value (α_2 to unity last). For values of α_1 above about

5.0, method (2) brought about irregular yielding of the rubber. Deformation (2) is arbitrary, since the dependence of α_2 on α_1 throughout the deformation will depend on the initial dimensions of the sheet. The initial dimensions were, however, the same for all specimens.

The specimens deformed by the constant α_2 method have crystallinities which are higher than those in simple extension at the same α_1. [Figure 5, curve (*b*); data from Figure 4.] Moreover, these specimens show little alteration in crystallinity on heating at 90° C in a vacuum for one hour and cooling at room temperature for twenty-four hours. 90° C is the highest temperature to which rubber at $\alpha_1 = 5.0$ can be heated without rupture occurring.

A few determinations were carried out to study the effect of heat on specimens deformed in pure shear with α_2 to unity last. These determinations were not so extensive or so accurate as those on unheated specimens, and only general remarks can be made. After heating a specimen deformed to $\alpha_1 = 5.5$ for about thirty minutes and cooling to room temperature, there was no immediate attainment of a significantly greater crystallinity. This only appeared on standing for one or two days. On subsequent heating, however, for a further thirty minutes, the attainment of high crystallinity on standing is much more rapid. Successive heat treatments, although promoting rapid attainment of equilibrium on cooling, tend to lower the optimum crystallinity, presumably because of thermal or oxidative degradation of the material. The optimum crystallinity attained by heat treatment was usually only about one-half of that attained in pure shear deformation by the α_2-constant method.

CRYSTALLITE ORIENTATION

The most usual estimates of tangential angular spread of crystalline-type reflections are $\phi_{\frac{1}{2}}$ values, that is, angles measured from the reflection center ($\phi = 0$) to a point where the intensity falls by half, or $\bar{\phi}$ values given by:

$$\bar{\phi} = \int_{-180°}^{+180°} I_\phi d\phi / I_0$$

where I_ϕ is intensity at ϕ.

Few quantitative estimates have been made previously. Goppel[12] quotes $\phi_{\frac{1}{2}}$ values for a number of rubbers in simple extension without correction for the finite width of the incident beam. A correction was used in the present case, based on that due to Jones[13] for θ-broadening, except that, instead of a powder, a crystal plate of mica giving a single reflection at about the same Bragg angle of 14° was used to estimate the corrected $\bar{\phi}_\beta$ of the (200) reflection (unit cell due to Bunn[14]). Profiles of both rubber and mica reflections recorded on an 11.46 cm. radius camera were almost Gaussian, so that the Gaussian correction curve of Jones was used.

Ten $\bar{\phi}_\beta$ values were determined on heated and unheated specimens in simple extension and in pure shear (constant α_2 deformation) in the range α_1 4.00 to 6.80. All the results were similar in magnitude, lying between 6.7° and 9.1°. The scatter of the points prevented the deduction of definite conclusions regarding the dependence of $\bar{\phi}_\beta$ on α_1. In general, heat treatment appeared to improve $\bar{\phi}_\beta$ in the more highly extended specimens by about 1.5°, in accord with the one observation of Goppel and Arlman[10] for simple extension.

Specimens deformed in pure shear with α_2 to unity last show marked orientation effects which parallel the changes in crystallinity, i.e., on heating, orientation improves but does not reach that attained for constant α_2 deformation.

An objection which might be raised concerning $\bar{\phi}_\beta$ measurements for pure shear is that, although the extended (α_1, α_2) plane was mounted normal to the x-ray beam, the $\bar{\phi}_\beta$ measurements do not refer to this plane, owing to the Bragg condition $2\theta = 14°$. A specimen was therefore mounted with its extended plane set at 83° to the direct beam on the reflection side. No significant difference in $\bar{\phi}_\beta$ could be detected[15].

COMPARATIVE VOLUME CHANGES

Volume changes for simply-extended rubbers of this type have been determined by Stern[3] using the method described by Gee, Stern and Treloar[16]. The unit cell of Bunn[14] gives a density for fully crystalline rubber as 1.008 g per cc. Taking Stern's value for the amorphous rubber as 0.9184g per cc. the relation between percentage crystallinity c and percentage volume change $100\,\Delta V/V$, is:

$$c = 11.2\ (100\,\Delta V/V)$$

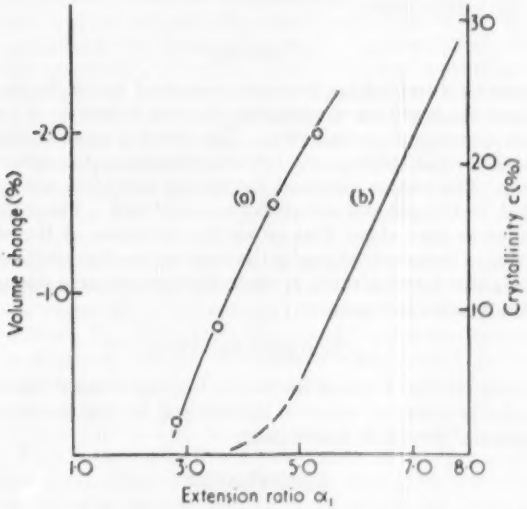


FIG. 6.—Comparative volume and x-ray measurements (a) Stern's results; (b) x-ray results.

The crystallinities calculated from volume changes are plotted together with x-ray crystallinity values (from Figure 4) in Figure 6. There is a considerable difference between the two sets of results.

The only other reported correlation using Bunn's data is that due to Arlman[17] on undeformed, unvulcanized rubbers which had crystallized on standing. The crystallinities calculated from density measurements were in exact accord with those determined by the x-ray method.

DISCUSSION

The dependence of crystallinity and of orientation on α_1 in simple extension is in full agreement with Goppel's determinations[2] for comparable rubbers. Crystallinity values of Field[1] must be considered too high, probably as a result of unsatisfactory exposure standardization.

No explanation is offered for the greater crystallinity in pure shear than in simple extension at the same α_1. The comparatively small difference in orientation for the two deformations is unexpected. A rapidly increasing dependence of $\bar{\phi}_\beta$ on α_2 is to be anticipated for α_2 values greater thn unity, since in two-dimensional extension ($\alpha_1 = \alpha_2 = \alpha$; $\alpha_3 \simeq \alpha^{-2}$), ϕ_β is 360°.

The effect of heat treatment on simply extended rubber and on specimens deformed in pure shear by the constant α_2 method could be due to their being in a state of genuine equilibrium crystallinity, and the behavior of heated specimens deformed in pure shear by the alternative route tends to support this view.

The irregular yielding of specimens subject to increasing α_2 could be simply explained in terms of disruption of the initial crystallinity.

It seems unlikely that the large difference in crystallinity as estimated from volume changes could be attributed to error in the assumed density for fully crystalline rubber. The difference may be due to the presence of small or disordered regions of crystallization, but more correlative determinations are required to settle this point.

SUMMARY

A vulcanized natural rubber has been deformed in simple extension and in pure shear and the resulting diminution of x-ray intensity of the amorphous halo used as a measure of crystallinity. The effect of mode of deformation and attempts to reach equilibrium states by heat treatment at constant deformation are described. The values obtained for simple extension are in accord with those reported by Goppel and not with those of Field. The degree of crystallinity is greater in pure shear than in simple extension at the same principal extension ratio. Corrected values for the orientation of crystalline regions have been obtained, and a comparison is made between volume changes and x-ray measurements for simple extension.

ACKNOWLEDGMENT

I am grateful to Dr. J. Stern for use of his unpublished data. This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Field, *J. Applied Physics* **12**, 23 (1941).
[2] Goppel, *Applied Sci. Research* [A]**1**, 3 (1949).
[3] Stern, J., unpublished results (1951).
[4] Compton and Allison, "X-Rays in Theory and Experiments", Van Nostrand and Co., N. Y., 1935, p. 189.
[5] Gee, *Trans. Faraday Soc.* **42**, 585 (1946).
[6] Manufactured by Unicam Instruments, Ltd., Cambridge, England.
[7] Simard and Warren, *J. Am. Chem. Soc.* **58**, 507 (1936).
[8] Industrial B-type, manufactured by Ilford, Ltd.
[9] Manufactured by Hilger and Watts, Ltd., London, England.
[10] Goppel and Arlman, *Applied Sci. Research* [A] **1**, 462 (1949).
[11] Mark and van Susich, *Kolloid.-Z.* **46**, 11 (1928).
[12] Goppel, *Applied Sci. Research* [A] **1**, 18 (1949); Goppel and Arlman, *Applied Sci. Research* [A] **1**, 462 (1949).
[13] Jones, *Proc. Roy. Soc.* (London) [A] **166**, 16 (1938).
[14] Bunn, *Proc. Roy. Soc.* (London) [A] **180**, 40 (1942).
[15] This lack of detectable difference is now known to be due to the relatively poor extent of higher orientation in pure shear (cf. Nyburg, *Acta Cryst.* **7**, 385 (1954)).
[16] Gee, Stern, and Treloar, *Trans. Faraday Soc.* **46**, 1101 (1950).
[17] Arlman, *Applied Sci. Research* [A] **1**, 347 (1949).

NATURE OF STARK RUBBER*

DONALD E. ROBERTS AND LEO MANDELKERN

RUBBER SECTION, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

INTRODUCTION

Long-chain molecules that possess a sufficient amount of chain regularity are capable of crystallizing under favorable conditions. The crystallization and the subsequent melting are similar to the processes that occur in monomeric materials of low molecular weight. The existence of an equilibrium melting temperature in polymers has been demonstrated[1]; it has also been shown that this temperature is systematically depressed by low molecular weight diluents in a manner quantitatively describable by the application of the thermodynamics of phase equilibria[2]. Similarly, the kinetics of crystallization of polymers can be satisfactorily accounted for by the assumption of the concurrence of nucleation and growth, with the magnitude of the nucleation rate dependent mainly on the difference between the equilibrium melting temperature and the temperature of the crystallization[3]. The success achieved in describing both the melting process and the crystallization kinetics gives additional evidence for the existence of an equilibrium melting temperature, and adds to its significance in the understanding of the crystallization behavior of polymers. This temperature is defined as the one at which the most perfect crystallites are unstable relative to the undeformed, unoriented liquid state.

For many polymers, including natural rubber, it has been observed that the melting temperature, T_m, depends on the crystallization temperature when the heating rate is relatively rapid[4]. However, for polyesters[5], polyamides[6], and more recently for natural rubber[7], it has been demonstrated that, when slow heating rates are employed, the melting temperature observed is independent of previous thermal history and then the equilibrium melting temperature is approached. This heating schedule is presumably conducive to the formation of more perfect crystallites, which are stable at higher temperatures. For natural rubber, the equilibrium melting temperature has been found[8] to be 28° (±1°) C. Melting temperatures appreciably higher than 28° C have also been reported for natural rubber. Considerable confusion has arisen, due to the apparent variability of its melting point. Since the melting temperatures below 28° C have been demonstrated to be solely a result of the heating rates used in their determinations, the occurrence of melting temperatures above 28° C also requires explanation.

The natural-rubber samples that have been observed to be high melting can be divided into two types, racked rubber and stark rubber. If unvulcanized natural rubber is repeatedly extended at an elevated temperature and then cooled, it can be given an enormous pseudopermanent extension without any applied force being maintained[9]. Extensions as great as 10,000 per cent have been reported. Rubber thus treated has been termed "racked" rubber, and its mechanical properties are similar to those of a hard inelastic material. The

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 54, No. 3, pages 167–176, March 1955.

racking process is accompanied by increase of density of the rubber, and its x-ray diffraction pattern gives a very intense fiber-type diagram, indicating not only that crystallization is occurring, but that the crystallites thus formed are highly oriented in the direction of the stretching. On heating, racked rubber retracts and the x-ray pattern disappears, indicating that fusion is occurring. The melting temperature, which depends on the extent of racking, occurs in the range 35° to 50° C, substantially higher than the equilibrium melting temperature assigned to natural rubber. However, as the crystallites are highly oriented in racked rubber, the connecting amorphous regions must be deformed from their statistically more probable configuration, and so the crystallites will be expected to be stable at higher temperatures than crystallites in an undeformed system.

When natural rubber is stored in temperate climates, it is occasionally found to be hard and inelastic, because of the development of appreciable amounts of crystallinity. Many of these samples also exhibit high melting points on initial heating and this type of rubber has been designated as "stark" rubber because it is hard and rather rigid at room temperature. Stark rubber has not heretofore been prepared under controlled conditions, and the reasons for its higher melting temperature cannot be ascertained from existing information, as in the case of racked rubber.

In an effort to understand the nature of stark rubber and the reasons for its high melting temperature, the melting behavior and x-ray diffraction patterns of four stark-rubber samples, from widely different sources, have been investigated. As a result of this study, some conclusions have been reached both as to the reasons for its high melting temperature and as to how it is formed. As a further consequence of these studies, methods have been devised for the laboratory preparation of stark rubber under controlled conditions.

EXPERIMENTAL PROCEDURE

The specific volume temperature relations and the melting temperatures were determined, using dilatometric techniques. Descriptions of the volume dilatometers employed, and the procedures followed have been published[10]. The dilatometers were immersed in constant-temperature baths controlled within ±0.1° C. The thermal histories of the samples and the times held at the various temperatures are detailed below. The absolute densities of the stark rubber specimens were determined at 25° C by the method of hydrostatic weighings[11].

The samples for the x-ray diffraction studies were cut from the sheets of stark rubber into rectangular strips about 1 mm thick. The x-ray diffraction photographs were taken in a flat-plate camera, using copper radiation (Kα) and operating at 40 kv and 20 ma. The sample-to-film distance was 10 cm., the aperture of the sample holder was 0.025 in., and the exposure time was 5½ hours. The variation in intensity of the diffraction around the circumference of a ring was determined by the manual use of a densitometer.

SAMPLES

Sample I was received from G. S. Whitby about 1936. It was a sample of smoked sheet, identified by the year of its preparation, 1913, and appeared to be similar to a specimen referred to in the literature[12]. Sample II was also a smoked sheet and had been highly milled, with the intention of using it as a rubber cement. It was stored in the basement of the Geophysical Laboratory

of the Carnegie Institution of Washington from 1936 until 1951, when it was discovered to have become stark. Sample III was received in 1929. It had been tapped and smoked on the Upper Amazon River and washed and dried at Belem (Para). The sample was firm when received, but not so stiff as it had become by 1952, when it was reexamined. Sample IV was from a bale of smoked sheet that had been stored in the NBS Rubber Section for several years; a portion of this bale was found to be stark, whereas other portions, including regions contiguous to the stark portion, were completely amorphous.

RESULTS

CHEMICAL ANALYSES

The results of chemical analyses for major components, which were performed on three of the stark rubber samples are given[12] in Table 1. The

TABLE 1

CHEMICAL ANALYSES OF STARK RUBBERS

Major component	Sample I %	Sample II %	Sample III %
Rubber hydrocarbon[a]	94.1	94.7	94.8
Acetone extract	3.3	3.5	2.6
Benzene insolubles	1.2	0.9	1.1
Protein[b]	2.1	2.3	2.5

[a] Chromic acid oxidation method.
[b] Boric acid method.

amounts of the major components found are typical of the composition of unpurified raw rubber. Hence the behavior of stark rubber cannot be attributed to any major chemical differences from the usual, or normal, raw rubber.

MELTING BEHAVIOR

The melting behavior of the four stark-rubber samples was investigated. Because of time effects above 35° C, a revision was required in the heating schedule that has been used with ordinary natural rubber[7] and other polymers[14]. The observations were initiated at about 15° C, and the temperature was raised at the rate of 1° each 12 to 24 hours. Up to temperatures of about 35° C, volume equilibrium appeared to be attained simultaneously with temperature equilibrium, and the specific volume varied linearly with temperature. This is in marked contrast to other polymers[15], in which partial melting and recrystallization always occur in the temperature range below the equilibrium melting temperature. At a given temperature above 35° C, the volume of the stark rubber samples no longer remained invariant with time, but was observed to increase slowly. These slow increases in the volume of stark rubber in this temperature region have also been observed by Whitby[12]. Although the rate of volume increase was slow, the total volume change at a given temperature was significant. A typical example of this phenomenon is that, for Sample I after 500 hours at 37° C, the specific volume had increased 0.0135 cc. per g. After the temperature was raised to 38° C and held there for 240 hours, the specific volume had increased 0.00318 cc. per g. Similarly, after 600 hours at 39° C it had increased 0.0030 cc. per g., and after 500 hours at 39.5° C it had

increased 0.0008 cc. per g. These observations are also in marked contrast to the behavior of other polymers for which, in the vicinity of T_m, only very slight increases in volume with time are observed. These observations for stark rubber necessitated that the samples be held for exceptionally long periods of time in the temperature interval between 35° C and T_m. In this interval the temperature was raised in 1° increments, and the sample was held at a given temperature until there was no perceptible increase of volume for about 5 to 7 days. Thus, the total heating process for a typical determination of T_m was of the order of 50 to 100 days. The melting temperature was then taken as the temperature at which the last trace of crystallinity disappeared, following the typical heating schedule just described.

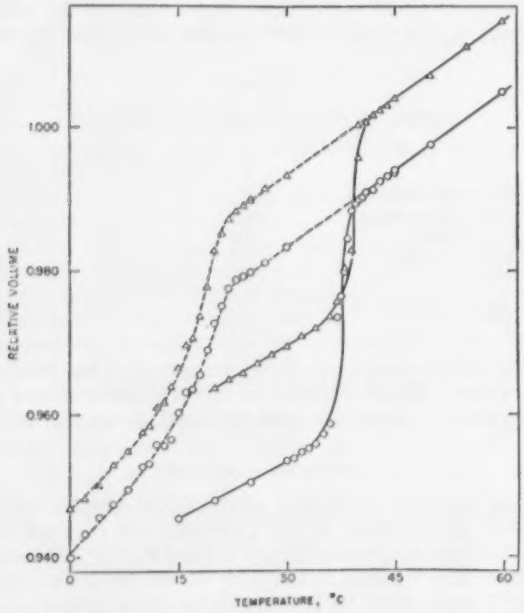


FIG. 1.—Relative volume-temperature plot for stark rubber. Solid lines, original heating; dashed lines, heating after initial melting and then crystallizing at 0° C; ○, sample I; △, sample II.

Possible reasons for this rather unusual melting behavior will be discussed in more detail in connection with the x-ray diffraction analysis of the structure of stark rubber. It is apparent that the value observed for T_m will depend on the over-all rate of heating and on the total time held at specified temperatures just below T_m. For example, Sample II was initially held in the temperature range of 37° to 41° C for 26 days; T_m was found to be 41° C, and the total volume change in melting was 0.0250 cc. per g. Another specimen of Sample II was brought from 30° to 38° C in 7 days, and up to the present has been held at 38° C for a little over a year. A steady increase of the volume has been observed, and 60 per cent of the total volume change occurring on melting the first specimen has already occurred. There is thus the distinct likelihood that if a sample

TABLE 2

DENSITIES AT 25° C AND MELTING TEMPERATURES OF STARK RUBBERS

Sample	ρ_{sw}	ρ_{ac}	$\Delta\rho$	T_m
				° C
I	0.9405	0.9129	0.0276	39.5 to 40
II	.9302	.9094	.0208	41
IV	.9270	.9092	.0178	42.0
III	.9114	.8945	.0169	45.5

of stark rubber is held at a temperature below the reported T_m for a sufficiently long time, a lower melting temperature will be observed[12].

Plots of the relative volume as a function of temperature are given in Figure 1 for Samples I and II. This figure also shows the curves that are obtained for

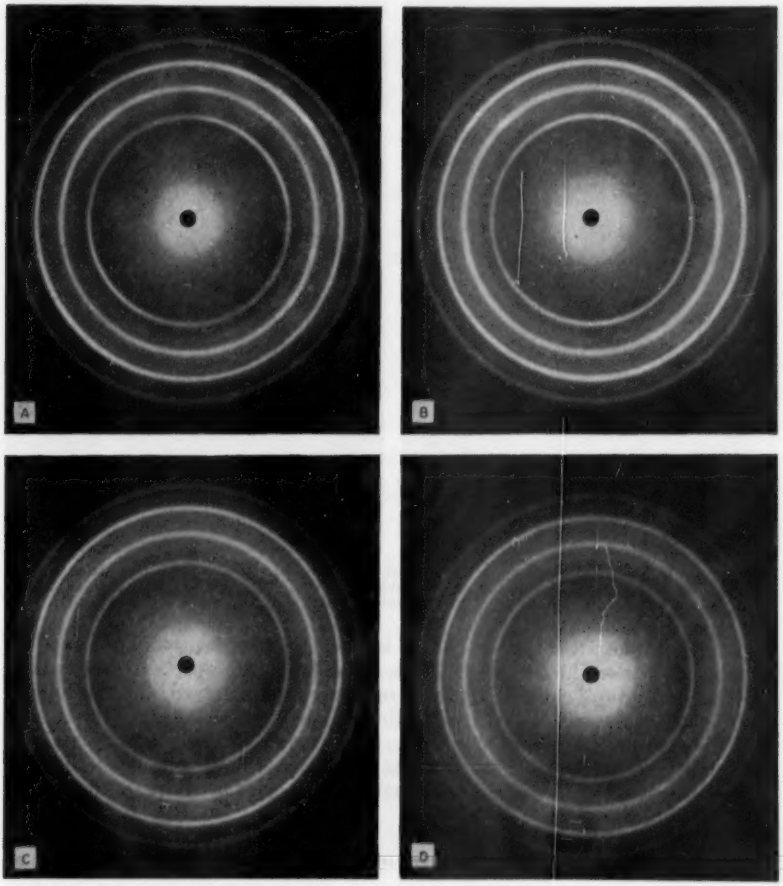


FIG. 2.—X-ray diffraction photographs of stark rubber. A and B, Sample I, with position of x-ray beam parallel and normal, respectively, to plane of rubber sheet; C and D, sample II, with position of x-ray beam parallel and normal, respectively, to plane of rubber sheet.

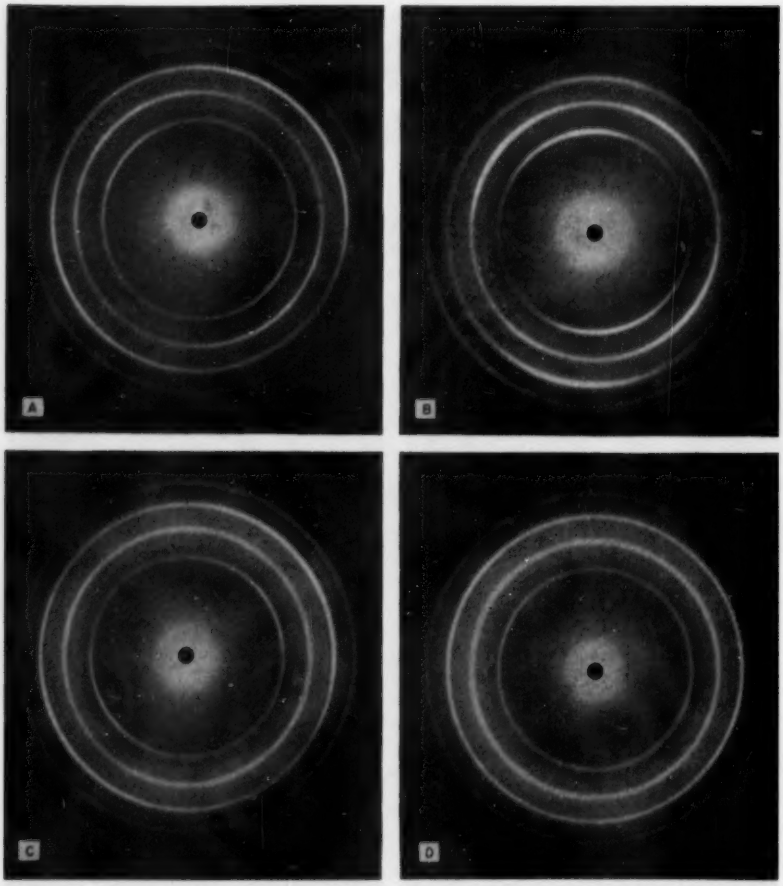


FIG. 3.—X-ray diffraction photographs of stark rubber. A and B, Sample III, with position of x-ray beam parallel and normal, respectively, to plane of rubber sheet; C and D, sample IV, with position of x-ray beam parallel and normal, respectively, to plane of rubber sheet.

the same samples after they were first melted and then recrystallized at 0° C. For the latter case, the melting behavior is similar in all respects to that usually observed for natural rubber. If stark rubber is first dissolved, and the solvent is sublimed or evaporated off, and if the sample is recrystallized at 0° C and slowly heated, the usual type of behavior is also found[7]. Thus, if the crystallites originally present in stark rubber once disappear, subsequent crystallization induced by cooling is identical with that which occurs in ordinary amorphous natural rubber.

MELTING TEMPERATURES AND DENSITIES

In Table 2 the densities of the semicrystalline rubber, ρ_{sc}, the completely amorphous rubber after melting the same samples, ρ_a, and their differences at

TABLE 3

SPACINGS FOR STARK RUBBER

d-spacing	Indexes[a]
6.30	200
5.00	201
4.24	120
3.77	{121 {121

[a] For a unit cell of dimensions *a*, *b*, and *c*, the direction of the chains (the fiber axis) is the *c* axis in the above.

25° C are given, as well as their respective melting temperatures, T_m, which were determined from the specific volume-temperature studies. As the stark rubber samples are almost identical in chemical composition, the variations in the density differences must reflect variations in the degree of crystallinity. The fact that the samples, when arranged in order of decreasing density differences, as in Table 2, are also in order of increasing melting temperatures may be regarded as fortuitous, because the range of melting temperatures is only a little larger than the precision of determination. Therefore, the authors are of the opinion that the melting temperature does not depend on the amount of crystallinity.

X-RAY DIFFRACTION

Typical x-ray diffraction patterns are illustrated in Figures 2 and 3. The positions of the four most intense rings correspond to the *d*-spacings given in Table 3 and confirm the values given by Barnes[16], for stark rubber and that

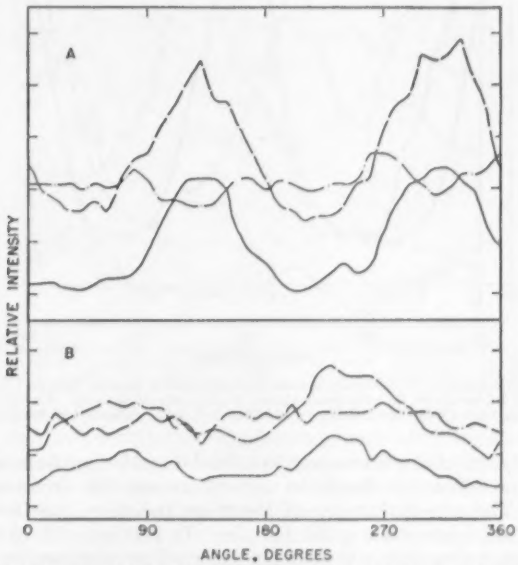


FIG. 4.—Relative intensity of diffraction around circumference of rings. A, Sample I, x-ray beam parallel to plane of rubber sheet; B, sample II, x-ray beam normal to plane of rubber sheet. Curves correspond to the following *d*-spacings: ——, 6.30; ·—·, 5.00; – –, 4.24. The unit of relative intensity is 0.1.

given by Clark, Wolthuis, and Smith[17] for rubber crystallized by either stretching or cooling. Thus, the crystalline form present in stark rubber is the same as that obtained on cooling amorphous natural rubber.

An inspection of the x-ray patterns indicates that, around certain of the rings, the intensity of the diffracted x-ray is not uniform. This is seen most clearly in the patterns for Samples III and IV (Figure 3). If the crystallites

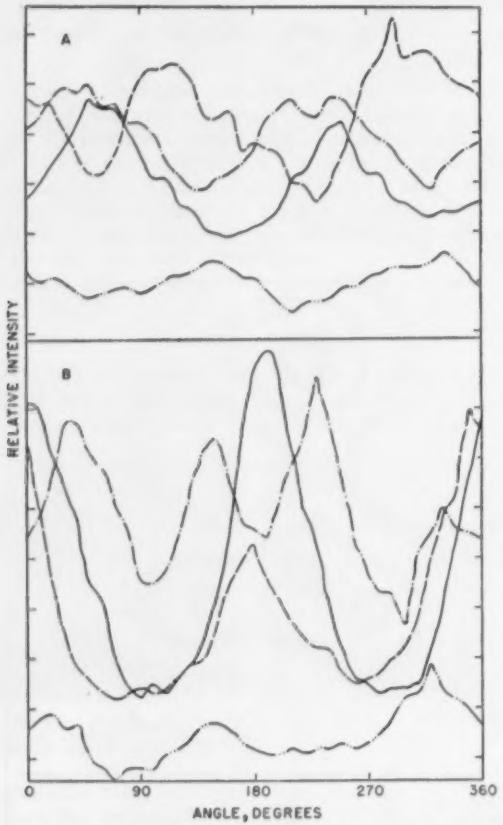


FIG. 5.—Relative intensity of diffraction around circumference of rings for Sample III. A, X-ray beam parallel to plane of rubber sheet; B, x-ray beam normal to plane of rubber sheet. Curves correspond to the following d-spacings: ——, 6.30; ·—·, 5.00; – –, 4.24; ··—, 3.77. The unit of relative intensity is 0.1.

were randomly oriented with respect to a fixed direction in the sample, then the intensity of the diffraction should be uniform around the circumference of any given ring. The non-uniformity of the rings indicates that the crystallites have a preferred orientation in the sample. To further confirm the reality of the orientation, a direction in the sample was fixed as reference, and the diffraction photographs were taken with the x-ray beam successively normal to and parallel to this direction. The results shown in Figures 2 and 3 indicate that

the diffraction patterns depend on the position of the beam relative to the sample, and hence the non-uniformity of the rings is caused by diffraction from oriented crystalline planes.

To further illustrate these observations, the variations of the relative intensity around the circumferences of the diffraction rings of interest are plotted in Figures 4, 5, and 6. For all the samples, the major variation of intensity occurs in the rings corresponding to reflections from the 200 and 120 planes, which are the only diffracting planes parallel to the direction of the chain axis. In

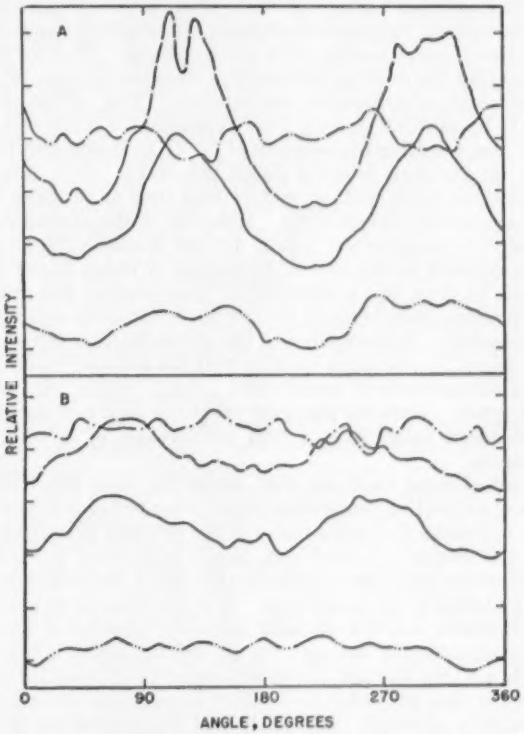


FIG. 6.—Relative intensity of diffraction around circumference of rings for sample IV. A, X-ray beam parallel to plane of sheet; B, x-ray beam normal to plane of sheet. Curves correspond to the following *d*-spacings: —, 6.30; ·—·, 5.00; ——, 4.24; ··—, 3.77. The unit of relative intensity is 0.1.

Sample II the effect is smaller than in the other samples, but the results are reproducible and well within the experimental limits of the photometering procedure. Figures 5 and 6 indicate clearly the non-uniformity of the rings and the changes in intensity that occur when the position of the x-ray beam relative to the sample is altered. More than two diffraction photographs for each sample are required to establish the detailed nature of the orientation. It is hoped that an analysis of the more detailed x-ray work now in progress will lead to a more quantitative description of the orientation. For present purposes, the establishment of the fact that the crystallites in stark rubber are oriented suffices.

DISCUSSION

It has been suggested that there are two forms of crystalline natural rubber, and that one of these forms is the higher-melting stark rubber[18]. However, the x-ray analyses of a sample of stark rubber by Barnes[16], the results of which are corroborated by the present work, indicate that the structure of the crystals in stark rubber is identical in all major respects with the structure of crystals induced by either stretching or cooling the amorphous rubber. Hence, polymorphism does not appear to be an explanation of the nature of stark rubber.

Wood and Bekkedahl[19] observed that, when natural rubber is crystallized by cooling, the melting temperature depends very markedly on the temperature of crystallization if rapid heating rates are employed. This led them to make the suggestion that the melting temperature observed in stark rubber is caused by a relatively high crystallization temperature. The validity of this suggestion is difficult to establish directly from experiment. Natural rubber crystallized at 14° C has a melting temperature of 28° C; to accomplish the crystallization at this temperature requires about 200 days. Crystallization at any higher temperature takes such an unduly long time as to make the necessary experiments a practical impossibility. However, in this temperature range the crystallization rate is governed mainly by the steady-state nucleation rate[3]. The extreme slowness of the rate of production of stable nuclei indicates that the difference between the crystallization temperature and the equilibrium melting temperature must be small, so that the equilibrium melting temperature is being approached. From studies of the crystallization rates of other polymers in this region[3], it is thought unlikely that the assigned value of the equilibrium melting temperature of undeformed natural rubber can be raised more than a few degrees. Thus the possibility that the high melting temperature of stark rubber results solely from a high temperature of crystallization seems somewhat remote.

Pickles[20] noted some years ago that, under the same conditions of storage, certain bales of natural rubber seemed more prone to become hard than others. This led him to believe that some factor in the previous history of the material, particularly the plantation processing, might be causing the observed effect. The x-ray diffraction patterns indicate clearly that a characteristic of stark rubber is the orientation of its crystallites. It is not difficult to envisage how the plantation processing might eventually cause the presence of oriented crystallites. After coagulation of the latex, the amorphous rubber is rolled into sheets, and the sheets are then stacked one upon another in an irregular manner. The bale of rubber is then subjected to a rather large simple compressional stress, which is eventually removed. It is likely that this process can cause the amorphous segments to be preferentially oriented, and, because of the high viscosity of natural rubber, this orientation can persist for long periods of time at the usual storage temperatures when the external stresses are removed. Orientation of the chain segments will facilitate the rate of crystallization at temperatures where the crystallization rate is prohibitively slow for undeformed rubber.

Because the crystallites are oriented, the amorphous regions that connect them can also be oriented to some extent. If this orientation were maintained during the fusion process, then a crystalline segment would gain less entropy on melting than in the case where the amorphous region was completely random. Then for an oriented system the fusion would have to occur at a higher temperature than in an unoriented system. If the orientation were maintained, this could explain the higher melting temperatures observed for both stark and

racked rubber. However, it does not explain the observed peculiarities of the melting process nor the fact that all the stark rubbers have melting temperatures in approximately the same range. Furthermore, if unvulcanized natural rubber is crystallized by stretching and the external force maintained during the subsequent heating (thus maintaining the orientation during the fusion), much higher melting points are observed[21].

After stark rubber has been melted and then recrystallized by cooling, the melting temperatures that one subsequently observes are the same as for normal natural rubber. Thus the initial heating of the stark rubber samples to temperatures slightly above the tabulated T_m causes the orientation to disappear. During the heating process, and within the time scale of the experiments, a temperature may be reached where the segmental motions of the amorphous rubber become sufficiently great to cause a return to their more probable configurations. If this temperature is greater than the equilibrium melting temperature of the unoriented semicrystalline polymer, T_m^0, then crystallites that were thermodynamically stable above T_m^0 due to the orientation will now become unstable and will melt. Because the fusion process causes an increase of the specific volume, the uniqueness of the melting behavior of stark rubber can be explained by the fact that, at a temperature several degrees below the assigned T_m, but above T_m^0, the relatively large volume changes with time are a manifestation of the slow rearrangement of the amorphous regions. Because the increases of the volume with time occur at all temperatures between 35° C and T_m, the rearrangement process is extremely temperature sensitive. It would then be expected that, as long as no external forces are maintained, melting will occur in approximately the same temperature interval, irrespective of the amount and type of orientation.

It is interesting to note that in their study of the dimensional changes of unvulcanized natural rubber, using interferometric techniques, Wood, Bekkedahl, and Peters[22] observed that plastic flow occurred in the vicinity of 40° C. Similarly, Smith and Saylor[23] noted that the birefringence in natural rubber caused by induced strains (not crystallites) disappeared in the range 40° to 55° C. With the observation that the crystallites in stark rubber are oriented and with the above explanation for the melting behavior, it is clear that the assigned values of T_m are not thermodynamically significant. The assignment of an equilibrium melting temperature to the unoriented semicrystalline natural rubber would thus appear to be justified[7].

In principle, other crystalline polymers should display this behavior. Its common observation in natural rubber is due to a combination of circumstances. The high viscosity of amorphous natural rubber allows the orientation of the chain segments to be maintained for relatively long periods of time in the temperature range of interest. The lower limit of this temperature range is set by T_m^0. As long as T_m^0 is sufficiently low, as in the case of natural rubber, for the rate of amorphous segmental rearrangement to be slow, this phenomenon should be observed.

STARK RUBBER PREPARED IN A LABORATORY

Since stark rubber has not been prepared heretofore under controlled conditions, it is now thought possible to prepare it in the laboratory. One should seek conditions such that the crystallization occurs while the rubber is being deformed, and that when the external stresses causing the deformation are removed, the orientation will persist at temperatures above T_m^0. Carson[24]

was able to produce stark rubber by deforming a sample in a rubber-cutting machine and storing under slight pressure for nearly a year at temperatures between 5° and 35° C.

Early attempts in this direction were made by Smith and Saylor[23], who compressed a sample of amorphous natural rubber between aluminum plates for 6 months at −25° C. The resulting crystallites displayed definite orienta-

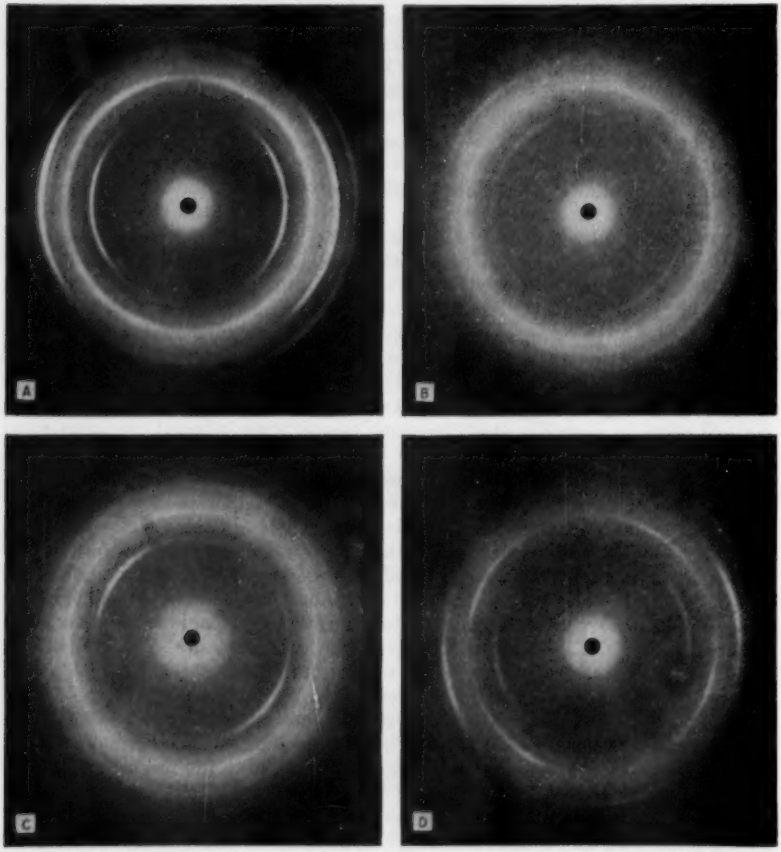


FIG. 7.—X-ray diffraction photographs of laboratory-prepared stark rubber. A, Prepared by McPherson and Holt; B, sprayed latex milled and rolled; C, cold-molding of Sample B; D, prepared in cast-iron pipe.

tion, but the melting point was only 10° to 11° C. A further experiment was performed wherein the rubber was compressed in a steel block at a pressure of 1000 atmospheres and held at −25° C for 2 weeks. Upon removal of the sample and on subsequent heating to room temperature, the rubber remained crystalline, and its melting point was found to be about 33° to 34° C.

About 1934 A. T. McPherson and W. L. Holt, then in the NBS Rubber Section, pressed some smoked sheet between aluminum-faced boards and then wrapped it very tightly with strips of stretched vulcanized rubber. Although

the details of the thermal history of the sample are not precisely known, the sample was kept most of the time in the temperature range 0° to 14° C. The sample was examined in May 1954, and found to possess an appreciable amount of crystallinity at 25° C. Dilatometric observations indicate that its melting temperature is greater than 35° C. In Figure 7,A, the x-ray diffraction photograph of this sample indicates very marked orientation.

A portion of a bale of sprayed latex, which contained about 95 per cent of rubber hydrocarbon and whose x-ray diffraction pattern indicated it to be completely amorphous, was passed through a mill several times and rolled into a tight cylinder. After storage at 25° C for 2 years, it was again examined and found to have lost some of its rubberlike elasticity. Its x-ray diffraction pattern is given in Figure 7,B, Although the intensity of the diffraction pattern is not great, it is evident that the crystallites are oriented. Because of the small amount of crystallinity developed, the melting point could not be determined precisely, but it is in the range 35° to 40° C. A portion of the roll was placed in a vacuum press at 28° C and subjected to a compressive load of 50 tons. The result of this treatment, as illustrated in Figure 7,C, was to further increase the amount of both crystallinity and orientation. The melting temperature of this specimen is 42° ± 2° C.

A small section of cast-iron pipe, which was closed at the lower end and threaded at the upper end, was completely filled with the amorphous sprayed latex. The upper end of the pipe was closed with a threaded cap and tightened completely, thus subjecting the rubber to a compressive stress with orientation of certain regions brought about in the process of tightening the cap. After storage at 14° C for 18 months, portions of the rubber had crystallized. They maintained their crystallinity after warming to room temperature. The x-ray diffraction pattern is illustrated in Figure 7,D, and its high orientation is apparent. The melting temperature was difficult to determine accurately, but it is in the vicinity of 35° C.

Stark rubber can thus be prepared in the laboratory by a variety of methods. Those discussed above are certainly not exhaustive, and other methods should be equally successful. The essential requirement seems to be orientation during the crystallization. This is a necessary, but not a sufficient, condition. In the course of this study, several methods that were attempted have not as yet yielded stark rubber. For example, holding samples at 14° C in simple extension at various extension ratios caused crystallization. However, when the tensile force was removed and the sample heated to 28° C, the crystallinity completely disappeared. Similarly, it is known from the work of Goppel and Van Rossem[25] that calendering rubber causes the crystallites that are formed on cooling to be oriented. However, when these experiments were repeated at the National Bureau of Standards a completely amorphous x-ray diffraction pattern was obtained at 25° C. The difference between these results and those of Goppel and van Rossem can be attributed to the fact that the diffraction photographs of the latter investigators were taken in the temperature range[26] 17° to 20° C. The apparent failure of the methods just described cannot be taken as final. It is possible that, after longer times, when greater amounts of crystallinity have developed, the rubber may become stark by the methods outlined.

Some additional samples of stark rubber are being studied, and other laboratory methods of preparation are being explored. The melting behavior of some of the stark-rubber samples reported in the present paper is being reexamined, using much slower heating rates.

SUMMARY

The melting behavior and x-ray diffraction patterns of four different samples of stark rubber have been investigated. The melting temperatures, 39° to 45.5° C, are substantially higher than that observed for natural rubber crystallized by cooling. The x-ray diffraction patterns indicate that the crystallites in stark rubber are oriented. This observation can explain the higher melting temperatures. Thus, the previous assignment of an equilibrium melting temperature, 28°(±1°) C, to unoriented crystalline natural rubber is shown to be appropriate. Several different methods that have been used successfully in preparing stark rubber under controlled conditions in the laboratory are outlined.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of G. Ugrinic and H. E. Swanson of the NBS Mineral Products Division for undertaking and accomplishing the x-ray diffraction work. Very helpful and interesting discussions of the problem were held with W. O. Baker and W. P. Slichter of the Bell Telephone Laboratories, and H. S. Kaufman of the M. W. Kellogg Co. L. A. Wood and N. Bekkedahl participated in many interesting discussions with the authors.

REFERENCES

[1] Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, **1953**, p. 563.
[2] Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, **1953**, p. 563; Flory, Garrett, Newman, and Mandelkern, *J. Polymer Sci.* **12**, 97 (1954).
[3] Mandelkern, Quinn, and Flory, *J. Applied Physics* **25**, 830 (1954).
[4] Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946); *J. Research Natl. Bur. Standards* **36**, 489 (1946); Rubber Chem. & Technol. **19**, 1145 (1946); Evans, Mighton, and Flory, *J. Am. Chem. Soc.* **72**, 2818 (1950); Flory, Hall, and Mandelkern, *J. Am. Chem. Soc.* **73**, 2532 (1951); Maynard and Mochel, *J. Polymer Sci.* **13**, 235 (1954); Rubber Chem. & Technol. **27**, 634 (1954).
[5] Evans, Mighton, and Flory, *J. Am. Chem. Soc.* **72**, 2818 (1950).
[6] Flory, Hall, and Mendelkern, *J. Am. Soc.* **73**, 2532 (1951).
[7] Roberts and Mandelkern, *J. Am. Chem. Soc.* **77**, 781 (1955).
[8] Maynard and Mochel, *J. Polymer Sci.* **13**, 235 (1954); Rubber Chem. & Technol. **27**, 634 (1954).
[9] Whitby, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, pp. 69 and 78.
[10] Flory, Hall, and Mandelkern, *J. Am. Chem. Soc.* **73**, 2532 (1951); Mandelkern and Flory, *J. Am. Chem. Soc.* **73**, 3206 (1951).
[11] Wood, Bekkedhal, and Roth, *J. Research Natl. Bur. Standards* **29**, 391 (1942); *Ind. Eng. Chem.* **34**, 1291 (1942); Rubber Chem. & Technol. **16**, 244 (1943).
[12] Whitby, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, p. 103.
[13] The authors are indebted to (Mrs.) R. J. Fanning for performing the chemical analyses.
[14] Flory, Hall, and Mandelkern, *J. Am. Chem. Soc.* **73**, 2532 (1951); Mandelkern and Flory, *J. Am. Chem. Soc.* **73**, 3206 (1951); Flory, Garrett, Newman, and Mandelkern, *J. Polymer Sci.* **12**, 97 (1954).
[15] Flory, Hall, and Mandelkern, *J. Am. Chem. Soc.* **73**, 2532 (1951); Mandelkern and Flory, *J. Am. Chem. Soc.* **73**, 3206 (1951); Flory, Garrett, Newman, and Mandelkern, *J. Polymer Sci.* **12**, 97 (1954); Roberts and Mandelkern, *J. Am. Chem. Soc.* **77**, 781 (1955).
[16] Barnes, *Can. J. Research* **15**, 156 (1937); Rubber Chem. & Technol. **10**, 462 (1937).
[17] Clark, Wolthuis, and Smith, *J. Research Natl. Bur. Standards* **19**, 479 (1937); *Rubber Age* (N. Y.) **42**, 35 (1937); Rubber Chem. & Technol. **11**, 32 (1938).
[18] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); Rubber Chem. & Technol. **8**, 5, (1935); Cotton, *Trans. Inst. Rubber Ind.* **16**, 303 (1941); Rubber Chem. & Technol. **14**, 762 (1941).
[19] Wood and Bekkedhal, *J. Applied Physics* **17**, 362 (1946); *J. Research Natl. Bur. Standards* **36**, 489 (1946); Rubber Chem. & Technol. **19**, 1145 (1946).
[20] Pickles, *India-Rubber J.* **67**, 69 (1924).
[21] Field, *J. Applied Physics* **12**, 23 (1941), Rubber Chem. & Technol. **14**, 555 (1941).
[22] Wood, Bekkedahl, and Peters, *J. Research Natl. Bur. Standards* **23**, 571 (1939); Rubber Chem. & Technol. **13**, 290 (1940).
[23] Smith and Saylor, *J. Research Natl. Bur. Standards* **21**, 257 (1938); Rubber Chem. & Technol. **12**, 18 (1939).
[24] Carson, *Ind. Eng. Chem.* **23**, 691 (1931); Rubber Chem. & Technol. **4**, 417 (1931).
[25] Goppel and van Rossem, *Physica* **9**, 213 (1942); Rubber Chem. & Technol. **19**, 403 (1946).
[26] Goppel, J. M., private communication.

BISALKYLATION THEORY OF NEOPRENE VULCANIZATION *

PETER KOVACIC

JACKSON LABORATORY, E. I. DU PONT DE NEMOURS & CO., INC.,
WILMINGTON, DELAWARE

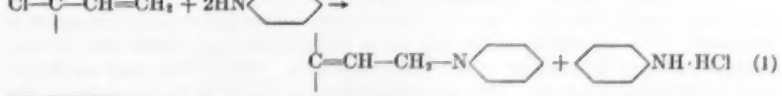
Among the organic compounds that are recommended[1] for use with magnesia and zinc oxide as vulcanizing agents for Neoprene are ethylenethiourea (2-imidazolidinethione), *p,p'*-diaminodiphenylmethane and the di-*o*-tolylguanidine salt of dicatechol borate. In the absence of sulfur, these agents in combination with zinc oxide do not vulcanize natural rubber. This points up a marked difference in the way these elastomers vulcanize. Although a major structural difference is the chlorine atom in Neoprene in place of the side methyl group in natural rubber, the small amount of tertiary allylic chlorine formed by 1,2-polymerization[2] is the important functional difference. The labile chlorine amounts to about 1.5 per cent of the total chlorine in a general-purpose Neoprene made at 40° C, such as Neoprene Type W used in this work. In Neoprene latex, this active chlorine is gradually liberated, and the polymer becomes cross-linked[3]. This paper demonstrates the importance of the labile chlorine in the vulcanization of dry Neoprene, accounts for the difference in the vulcanization of Neoprene and natural rubber, and suggests a bisalkylation theory of Neoprene vulcanization.

RESULTS AND DISCUSSION

Untreated Neoprene.—A small number (about 1.5 mole-%) of the monomer units in Neoprene are incorporated in the chain by 1,2-addition during polymerization[4].

1,4-addition 1,2-addition

The tertiary allylic chlorine in the 1,2-structure readily reacts with piperidine or aniline, with elimination of chloride ion (Table I). Nitrogen from the aniline or piperidine is present in the polymer in the ratio of one nitrogen atom for each chlorine lost. The reaction proceeds, therefore, by substitution, and an S_n2' mechanism[5] provides a logical explanation for the observations.



(1)

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 47, No. 5, pages 1090–1094, May 1955.

In contrast, practically no reaction resulted from treatment of Neoprene with triethylamine, pyridine, triethylamine-phenol, or pyridine-phenol in xylene for 14 hours at 100° to 112° C. This agrees with the results of Young, Webb, and Goering[6], who showed that triethylamine reacts much more slowly with α-methylallyl chloride than does diethylamine.

The small amount of labile chlorine in Neoprene is known[3] to be necessary for some types of vulcanization. Neoprene Type W usually is cured by an organic vulcanizing agent together with the oxides of zinc and magnesium. Among these organic vulcanizing agents are bifunctional compounds[7] of the types shown in Table II.

It is suggested that vulcanization of untreated Neoprene by these compounds proceeds through bisalkylation of the vulcanizing agent by the polymer chains

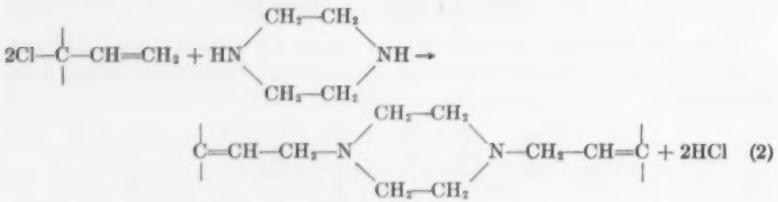
TABLE I

PREPARATION OF AMINE-TREATED NEOPRENE

Reagent[a]	Solvent	Temp. (° C)[b]	Cl removed (%)[c]	Polymer analysis (%)[d] Cl	N
—	Benzene	80 ± 2	Trace	39.4	0.02
Piperidine	Benzene[e]	80 ± 2	1.44	38.2[f]	0.27[f]
Aniline	Xylene	100–105	—	38.5	0.27

[a] Ratio of reagent to chloroprene unit, moles = 2.6.
[b] Time = 14 hours.
[c] Determined on aqueous extract and based on total available chlorine (37.5% of polymer).
[d] Untreated Neoprene Type W contains 37.5% chlorine and 0.02% nitrogen. Chlorine content is raised by precipitation from solvent because of removal of solvent-soluble, nonpolymeric components.
[e] Essentially same results were obtained by treatment in xylene at 100–105°.
[f] Values unchanged by repeated precipitation of polymer.

at the active chlorine positions. The cross-linking reaction in the case of piperazine is illustrated as follows:



The hydrogen chloride, which may initially form an amine hydrochloride, would be expected to react with zinc oxide or magnesium oxide, normally present, to form the corresponding chloride.

It is significant that the active agents listed in Table II, commonly referred to as accelerators, possess a structure capable of alkylation at two positions by an alkyl halide. In addition, the monofunctional compounds related to the bifunctional ones are inactive, e.g., phenol, *N*-methylaniline, and di-*n*-butylamine (Figure 1).

The limited number of cross-linking sites involving labile chlorine should result in a maximum in the cure as the concentration of the vulcanizing agent is increased, since monoalkylation will occur at high concentrations with formation of polymer side chains instead of cross-links. This is the case as shown with catechol in Figure 2. The position of the maximum in the modulus as the concentration of the vulcanizing agent is increased is in good agreement with the

TABLE II

NEOPRENE VULCANIZING AGENTS

Diamines

p,p'-Diaminodiphenylmethane
Piperazine
2,5-Dimethylpiperazine

Dihydric phenols or derivatives

Catechol
Di-*o*-tolylguanidine salt of dicathechol borate

Aminophenols

2-Methyl-4,6-bis(dimethylaminomethyl)phenol

Thioureas

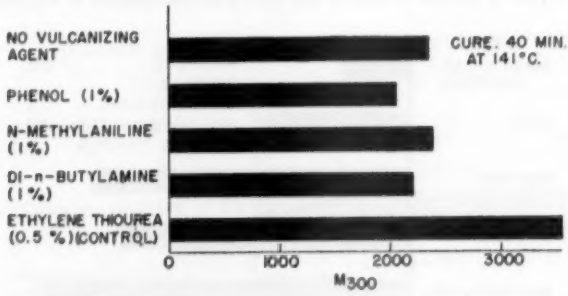
Ethylenethiourea
N,N'-Diphenylthiourea

Thioamides

ε-Thiocaprolactam

calculated value of 0.9 per cent catechol required for cross-linking with the 1.5 per cent active chlorine. A similar effect is noted[8] in vulcanization with 2-mercaptothiazoline at varying concentration.

According to the proposed mechanism, the appropriate bifunctional molecule alone should cross-link Neoprene. Busse and Billmeyer have shown that Neoprene dissolved in tetralin is gelled on heating with tetraethylenepentamine or ethylenethiourea[9], as well as with benzidine or piperazine hexahydrate[10], indicating that such cross-linking indeed occurs. However, in dry Neoprene in the absence of metal oxide, ethylenethiourea produced poorly cured stocks (Figure 3). This implies that, for practical cures, the cross-linking reaction requires a catalyst such as metal oxide or metal chloride. An alternative interpretation is that a combination of cross-linking reactions occurs with zinc oxide also present. Figure 4 shows the partial vulcanization of Neoprene Type W achieved with metal oxides alone. It is believed that this partial cure can be attributed to the formation by zinc oxide of ether cross-links at the active



Neoprene	100
N-Phenyl-2-naphthylamine	1
SRF carbon black	50
Magnesia	2
Zinc oxide	5

FIG. 1.—Monofunctional compounds as Neoprene vulcanizing agents.

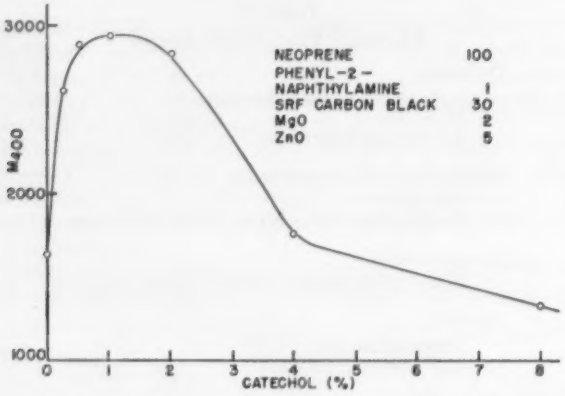


FIG. 2.—Relation of modulus to vulcanizing agent concentration.

chlorine positions, or to an ionic-type polymerization initiated by zinc chloride. Supporting evidence that zinc chloride plays a role, obtained with various types of Neoprene, is provided by the nature of cure retarders, which may be classified into two groups.

1. Those which compete with zinc oxide for hydrogen chloride, such as magnesium oxide and sodium acetate.
2. Those which reduce the catalytic activity of zinc chloride by coordination, such as water and aromatic secondary amines.

Amine-treated Neoprene.—The substitution of amine groups for the active chlorine in Neoprene causes a radical change of the vulcanization characteristics. The piperidine- and aniline-treated polymers described in Table I were not vulcanized by ethylenethiourea (Table III). Other bifunctional curing agents listed in Table II were also inactive in the piperidine-treated polymer. These compounds give M_{300} values of 2200 to 3200 pounds per square inch in untreated Neoprene. Furthermore, small amounts of piperidine compounded with Neoprene Type W similarly render the polymer insensitive to vulcanization by

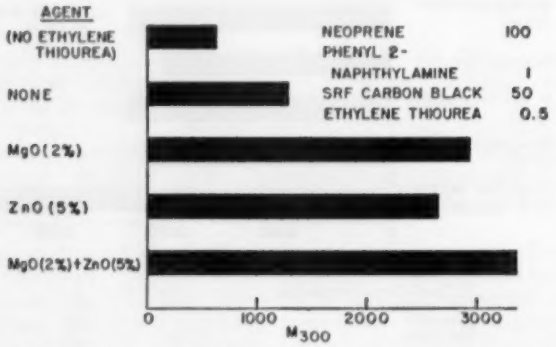


FIG. 3.—Effect of metal oxides on vulcanization with ethylenethioureas.

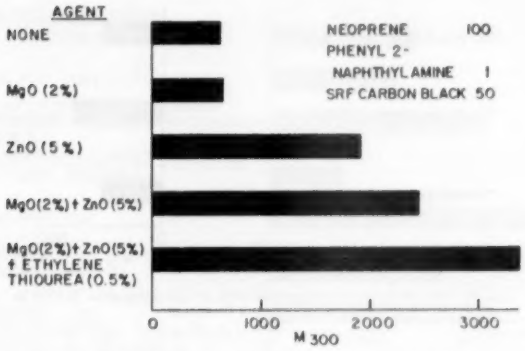


FIG. 4.—Effect of metal oxides on Neoprene vulcanization.

ethylenethiourea (Figure 5). Amine-treated Neoprene resembles natural rubber in its inertness to vulcanizing agents of this type. Piperidine-treated Neoprene is not vulcanized by ethylenethiourea, even on addition of zinc chloride or triphenylchloromethane (Figure 6). The importance of active chlorine attached to the polymer chain is thereby indicated.

TABLE III

VULCANIZATION BEHAVIOR OF AMINE-TREATED NEOPRENE WITH ETHYLENETHIOUREA

Neoprene	M_{200}: No vulcanizing agent	M_{200}: Ethylenethiourea, 0.5–1%
Untreated	1390	3150
Piperidine-treated	710	450
Aniline-treated	1650[a]	1550[b]

[a] Extrapolated. T_B = 940 lb./sq. in. at 230% elongation.
[b] Extrapolated. T_B = 990 lb./sq. in. at 220% elongation.

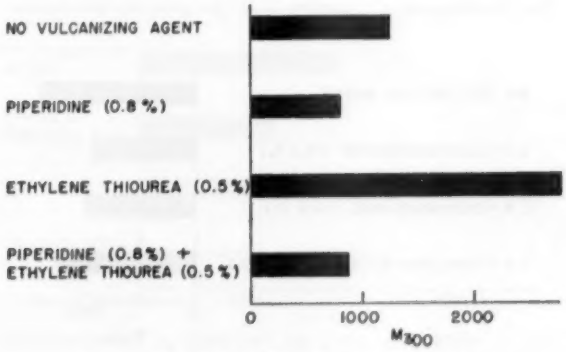


FIG. 5.—Effect of piperidine on Neoprene vulcanization.

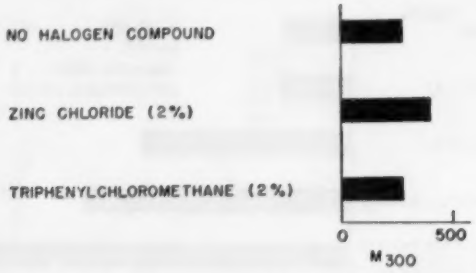


FIG. 6.—Active halogen compounds with ethylenethiourea (0.5%) in piperidine-treated Neoprene.

Piperidine-treated Neoprene can, however, be given a high state of cure by treatment with bifunctional agents of other types. Thus, it was possible to obtain moduli as high as 2900 pounds per square inch by the use of labile dihalides (Figure 7). These compounds are not vulcanizing agents for untreated Neoprene (Figure 8). It is reasonable to believe that cross-linking of the

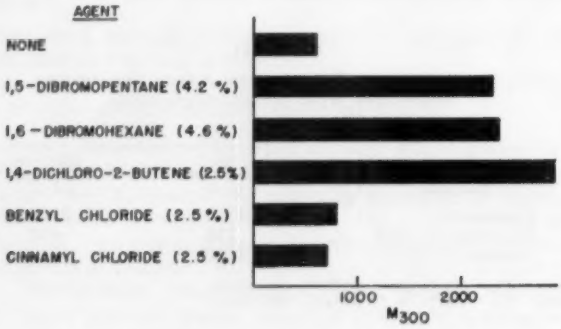


FIG. 7.—Vulcanization of piperidine-treated Neoprene with labile halides.

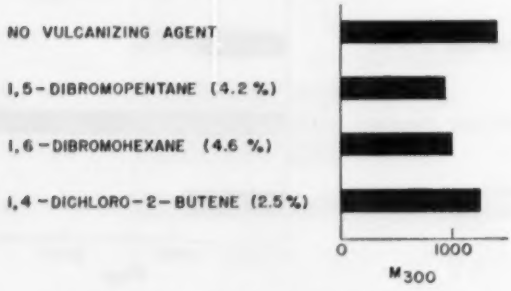


FIG. 8.—Effect of labile dihalides on untreated Neoprene.

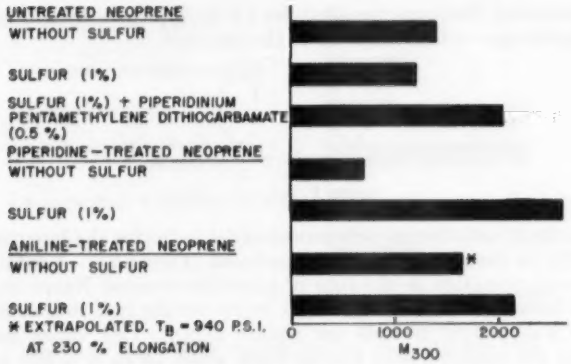
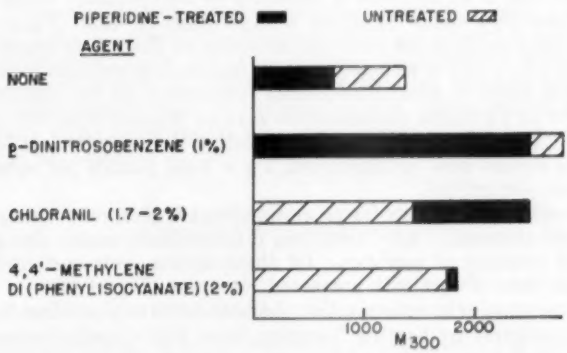


FIG. 9.—Sulfur vulcanization of untreated and amine-treated Neoprene.



4,4'-Methylene di(phenylisocyanate) extrapolated. T_B = 1200 pounds per square inch at 225% elongation.

FIG. 10—Vulcanizing agents for piperidine-treated Neoprene.

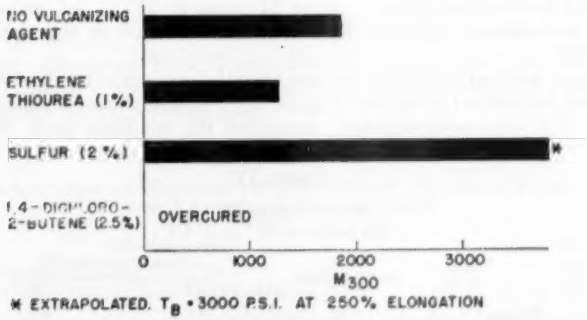
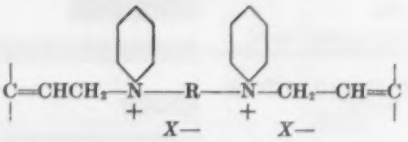


FIG. 11.—Vulcanization of polymer from dimethyl-amine-treated Neoprene latex.

piperidine-treated Neoprene by dihalides (X-R-X) occurs by a bisquaternization at the nitrogen-containing sites in the polymer.



The low order of activity of labile monohalides indicates the importance of bifunctionality in the active halogen component (Figure 7). A catalytic effect appears to be operative in the cure of piperidine-treated Neoprene with 1,4-dichloro-2-butene, as omission of metal oxides results in a substantially lower modulus (M_{300} = 1080 pounds per square inch). This value, however, is higher than the modulus with carbon black alone (M_{300} = < 300 pounds per square inch).

Sulfur alone is a poor vulcanizing agent for either Neoprene or natural rubber; addition of an activator is necessary for best results. With the amine-treated Neoprene, sulfur produces a high state of cure (Figure 9). The difference apparently arises from the presence, in the amine-treated polymer, of nitrogen which acts as an activator. Metal oxide is required for a high state of cure with sulfur in piperidine-treated Neoprene. In the absence of metal oxide, sulfur at 2 per cent concentration gave an M_{300} value of 1650 pounds per square inch, whereas with the usual formulation there resulted an M_{300} of 3200 pounds per square inch (extrapolated, T_B = 2400 pounds per square inch at 250 per cent elongation).

Other vulcanizing agents for piperidine-treated Neoprene were p-dinitrosobenzene and chloranil. 4,4′-Methylene di(phenylisocyanate) also produced a substantial increase of modulus. Of these agents, only p-dinitrosobenzene gave a high state of cure with untreated Neoprene (Figure 10).

A polymer similar in vulcanization characteristics to piperidine-treated Neoprene was prepared by heating Neoprene latex with dimethylamine. In this case also, reaction proceeded with incorporation of nitrogen into the polymer. Ethylenethiourea was inactive in the isolated polymer, whereas sulfur produced a high state of cure (Figure 11). 1,4-Dichloro-2-butene gave high-modulus, short-breaking vulcanizates.

Heat-treated Neoprene latex.—Labile chlorine can be removed from Neoprene merely by heating the latex[11]. After 24 hours at 95° C, 1.7 per cent of the chlorine theoretically present (40 per cent) was found in the aqueous phase (Table IV).

Polymer isolated from the latex was essentially uncured by ethylenethiourea. It was not vulcanized by sulfur (Figure 12), but addition of a sulfur activator, such as N,N'-diphenylguanidine, increased the modulus from 700 to 1900

TABLE IV

HEAT-TREATED NEOPRENE LATEX

(24 hours at 95° ± 2° C)

	Cl in aqueous phase (%)	Polymer analysis (%)	
		Cl	N
Before	0.65	39.5	0.01
After	1.71	38.4	0.02

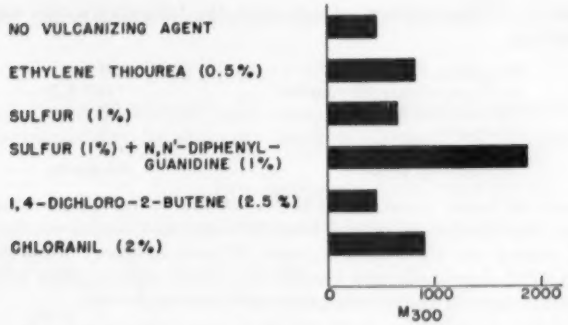
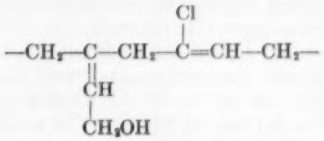


FIG. 12.—Vulcanisation of polymer from heat-treated Neoprene latex.

pounds per square inch. 1,4-Dichloro-2-butene did not produce cross-linking, a fact which may be attributed to the absence of easily alkylatable sites in this polymer. Chloranil showed poor vulcanizing activity. Both *p*-dinitrosobenzene and 4,4′-methylenedi(phenylisocyanate) gave short-breaking, high-modulus vulcanizates (Table V). In a previous publication[3] it was concluded that, during latex heat-aging, labile chlorine sites can undergo at least two types of reaction: substitution by hydroxyl groups and cross-link formation. Avidity of cure with a diisocyanate supports the proposal that hydroxyl groups are present in heat-treated Neoprene latex polymer, as illustrated.



Degree of cross-linking.—On the basis of the proposed theory of vulcanization by bisalkylation, it is possible to calculate the number of cross-links formed in Neoprene. The presence of 1.5 per cent active chlorine could result theoretically in one cross-link for every 67 chloroprene units. For Neoprene of 200,000 molecular weight, this would correspond to an average of 34 cross-links per molecule.

EXPERIMENTAL PROCEDURE

Materials.—Neoprene Type W and Neoprene Latex Type 735 were used in this work. Polyac rubber accelerator activator (25 per cent poly-*p*-dinitrosobenzene with an inert filler) was used.

TABLE V

VULCANIZATION OF POLYMER FROM HEAT-AGED NEOPRENE LATEX[a]
(Cure. 20 minutes at 153° C)

Vulcanising agent	T_S	E_B
p-Dinitrosobenzene (0.75%)	880	100
4,4′-Methylenedi(phenylisocyanate) (0.15%)	770	100

[a] For comparison, untreated neoprene vulcanized with 1% of piperazine hydrate gave the following moduli: M_{300}, 2100 lb./sq. in.; M_{100}, 300 lb./sq. in.

Evaluation.—Unless otherwise indicated, the following recipe was followed in compounding.

Neoprene	100
N-Phenyl-1-naphthylamine	0.9–1.6
SRF carbon black	30
Magnesia	4
Zinc oxide	5
Vulcanizing agent	As shown

In almost all cases, cures were effected at 153° C for 40 minutes.

Samples were prepared in the form of rings and tested on the Williams machine[12], except for those in Figures 1, 2, and 3, which were prepared as standard ASTM dumbbells and tested on a Scott tester. The following abbreviations are used in the presentation of stress-strain data.

M_{300}. Stress (pounds per square inch at 300% elongation)
T_B. Tensile strength (pounds per square inch at break)
E_B. Elongation at break

Amine-treated Neoprene.—A mixture of 3000 grams of a 10% benzene solution of Neoprene and 750 grams of piperidine (97% purity) was heated in an oil bath at the reflux temperature, with slow stirring, for 14 hours. A small amount of white crystalline solid collected in the gray-brown solution. The mixture was divided into two parts, and each was extracted with nine 200-cc. portions of distilled water. Chloride ion in the aqueous extract was determined by potentiometric titration. The combined benzene solution was coagulated with 3 liters of alcohol and the polymer washed with three 300-cc. portions of alcohol. The Neoprene was redissolved in benzene and precipitated two more times. In the case of water-insoluble reagents, e.g., aniline and triethylamine, the polymer was precipitated a total of four times. After being partially dried in air overnight, the polymer was compounded with about 1% of its weight of *N*-phenyl-1-naphthylamine at 40° to 50° C, washed on a mill at 40° C with water, and then milled to dryness at 70° C. The amber-colored product was similar in appearance and mill behavior to commercial Neoprene.

The *N*-phenyl-1-naphthylamine was omitted from samples taken for analysis. Analytical variations were as follows: chlorine (Parr method), ±0.5%; nitrogen (macro-Kjeldahl), ±0.02%.

Dimethylamine-treated Neoprene latex.—A mixture of 300 cc. of Neoprene Latex Type 735 and 300 cc. of 25% dimethylamine solution was heated under nitrogen in a steel bomb at 70° C for 10 hours. At the end, 1.4% of the chlorine was present as chloride ion. The polymer was coagulated by alcohol, water-washed on a mill, and dried on a mill at 70° C. It was swollen by benzene.

Analysis. Chlorine, 38.6; nitrogen, 0.21.

Heat-treated Neoprene latex.—Neoprene Latex Type 735 (600 grams) was placed under nitrogen in a closed bottle and kept in a water bath at 95° ± 2° C for 24 hours. After being cooled to room temperature, a thin surface skin of coagulum was removed, and a sample of the latex was analyzed for chloride ion by potentiometric titration. The latex was coagulated with 1 liter of alcohol and the polymer was washed with water on a mill. The polymer was white and tough and did not band readily. About 1% by weight of *N*-phenyl-1-naphthylamine was added on a mill at 50° C, and the polymer was milled to dryness at 70° C. Banding occurred after continued milling.

N-Phenyl-1-naphthylamine was omitted from the sample taken for analysis. Analyses are shown in Table IV. The treated polymer appeared to be slightly

cross-linked. It did not completely dissolve in benzene, but was greatly swollen.

ACKNOWLEDGMENT

The amine treatment of the latex was done by W. R. Remington. Retardation of Neoprene cure by aromatic secondary amines was studied by P. A. Sanders.

REFERENCES

[1] Catton, "The Neoprenes", Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Wilmington, Del., 1952.
[2] Maynard and Mochel, *J. Polymer Sci.* **13**, 251 (1954).
[3] Andersen and Kovacic, *Ind. Eng. Chem.* **47**, 171 (1955).
[4] Salomon and Koningsberger, *Rec. trav. chim.* **69**, 711 (1950); Andersen and Arnold, *Ind. Eng. Chem.* **45**, 2727 (1953); Maynard and Mochel, *J. Polymer Sci.* **13**, 251 (1954); Andersen and Kovacic, *Ind. Eng. Chem.* **47**, 171 (1955).
[5] Young, Webb, and Goering, *J. Am. Chem. Soc.* **73**, 1076 (1951); Andersen and Kovacic, *Ind. Eng. Chem.* **47**, 171 (1955).
[6] Young, Webb, and Goering, *J. Am. Chem. Soc.* **73**, 1076 (1951).
[7] Forman, Radcliff, and Mayo, *Ind. Eng. Chem.* **42**, 686 (1950); Neal, *Rubber Age* (N. Y.) **67**, 569 (1950); Radcliff, Mayo, and Fritz, Report No. 50-1 (1950), Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Wilmington, Del.; Baum (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,544,746 (Mar. 13, 1951); Catton "The Neoprenes", Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Wilmington, Del., 1952.
[8] Radcliff, R. I., personal communication.
[9] Busse and Billmeyer, *J. Polymer Sci.* **12**, 599 (1954).
[10] Busse, W. F., and Billmeyer, F. W., Jr., personal communication.
[11] Andersen and Arnold, *Ind. Eng. Chem.* **45**, 2727 (1953); Andersen and Kovacic, *Ind. Eng. Chem.* **47**, 171 (1955).
[12] Williams and Sturgis, *Ind. Eng. Chem.* **31**, 1303 (1939).

COMBINATION OF RUBBER AND CARBON BLACK ON COLD MILLING *

W. F. WATSON

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTS, ENGLAND

The mechanism for the degradation of elastomers by cold milling[1] can be represented by:

$R - R \rightarrow R. + R.$	Scission by shear forces
$R. + R. \rightarrow R - R$	Radical recombination
$R. + X \rightarrow RX.$ or $RY + Z.$	Radical acceptor reaction
$RX.$ or $Z. \rightarrow\rightarrow$	Termination to noncross-linked products

$R.$, $RX.$, or $Z. + R - R \rightarrow\rightarrow$ Termination to cross-linked products

where the term "radical acceptor" denotes a substance competing significantly with recombination.

Although the structure of carbon black is imperfectly known, x-ray analysis has shown it to consist of layers of condensed rings of carbon atoms. Unsaturation and discontinuities in the layers are likely to provide sites for attack of free radicals, and thus make carbon black a radical acceptor of a special polyfunctional type. Assuming combination of rubber radicals and carbon black, a particle could terminate more than one sheared rubber chain. Furthermore, rubber chains attached to a carbon black particle could also undergo scission by shear and be terminated by combination with other particles. The result anticipated from this picture is a network of rubber and carbon black held together by chemical bonds. In rubber solvents, such a network would be insoluble and merely become swollen gel.

Insolubilization of rubber on milling with carbon black has been reported on occasion, but the evidence is not sufficiently extensive to draw reliable conclusions as to its cause. This paper reports a systematic investigation of the occurrence of rubber-carbon black gel on cold milling. This gel has been shown to form, and the conditions for its formation and its properties have been interpreted as strong evidence for the above hypothesis of chemical-bond attachment of rubber and carbon black.

EXPERIMENTAL MATERIALS AND METHODS

Materials.—Deproteinized crepe of oxygen content <0.5%, nitrogen content <0.1%, and ash <0.1%, was kindly supplied by the Indonesian Rubber Research Institute. It was wholly soluble in benzene within 48 hours' standing at room temperature, giving an intrinsic viscosity, varying with the batch, of 4.8 to 5.2. Bleached pale crepe and yellow-circle smoked sheet were standard commercial products. Philblack-O was of British manufacture. The

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 47, No. 6, pages 1281–1286, June 1955. This paper was presented in part at the Third Rubber Technology Conference, London, England, June 22–25, 1954.

radical acceptors were laboratory grade chemicals, and were not further purified. Benzene was of analytical reagent quality.

Dispersion of carbon black in rubber.—The most interesting stage of the rubber-black interaction had already passed before carbon black could be incorporated in rubber by conventional addition during milling, for example, the minimum milling of deproteinized crepe to give a satisfactory dispersion of 50 parts of Philblack-O per 100 parts of rubber (by weight) on a 12-inch mill reduced the intrinsic viscosity from 5.5 to 0.9 and gave a gel content of 36 per cent, 31 per cent of which was insolublized rubber.

Ball-milling and then freeze-drying successfully dispersed carbon black in rubber without affecting rubber viscosity or producing rubber-carbon black gel. The following technique was adopted.

Ten grams of rubber were dissolved in 350 cc. of benzene in a ball mill, and 5 grams of carbon black was added. The viscous mass was ball-milled by ¾-inch screened pebbles for 16 hours at 60 r.p.m. The rubber acted as dispersing agent in the nonpolar solvent by virtue of both its aliphatic chain structure and its increasing of solution viscosity[2]. The liquid was decanted into a 3-liter flask, from which the benzene was removed by freeze drying over 48 hours. The resultant mixture was shown to contain carbon particles of colloidal dimensions by remaining indefinitely as a sol in viscous solution. Most of the carbon black could be flocculated, along with approximately 20 per cent of its weight of adsorbed rubber, on dilution to <1 per cent rubber.

Milling.—Millings in air were carried out on a laboratory mill with 12-inch rolls, 6 inches in diameter the front and back rolls rotating at 13.7 and 18.9 r.p.m., respectively, and with a clearance (nip) adjusted to 0.005 inch; 0.9-gram samples of rubber-carbon black mixtures were passed through the nip a given number of times, 5 seconds being allowed between each pass. The rolls were water-cooled to 18° to 25° C.

More precise temperature control was of no value because of the heat developed during deformation, the gel formation being independent of roll temperature in this range within the experimental error of its measurement. The roll temperatures recorded in the experimental section are, then, only of nominal value. One pass through the nip raised the rubber-carbon black temperature to over 60° C; the heat developed during deformation decreased on further milling, owing to softening of the rubber.

Millings under nitrogen were carried out in a small internal masticator[3]. Three grams of rubber-carbon black batches were masticated for known times in a 3- to 5-cc. chamber, through which nitrogen continuously flowed. The lower scroll rotated at 75 r.p.m. Water circulation at 30° C kept the average rubber temperature within 5° C of this value.

Measurement of gel.—The method adopted was similar to that for determining gel by cross-linking radical acceptors[1] and for the carbon gel produced on hot milling[4].

Weighed amounts of 0.4 to 0.6 gram of rubber-carbon black mixtures were suspended in 50 cc. of benzene for 6 days in the dark at room temperature. The time in benzene was chosen on finding that gel content remained constant from 4 to at least 14 days. The solutions were vigorously shaken each day.

Gel content was determined from sol concentration. With colorless solutions, known volumes of sol could be directly pipetted when the gel was a coherent mass; otherwise known weights of sol were collected after passing by gravity through a Grade-2 sintered-glass disk. Brown to opaque solutions were centrifuged for 2 hours at 13,000 r.p.m. in stainless steel tubes with poly-

thene caps. The clarified liquid portions were decanted from the packed-down deposists. The sol was freeze-dried for 48 hours at a pressure of less than 1 mm. of mercury for concentration determination. Reproducibility of gel content on the same sample of rubber-carbon black in different benzene suspensions was within 3 per cent. Variation of gel contents of samples separately masticated to the same extent was less than 7 per cent. Recorded gel contents are the mean of duplicate mastications.

For measurement of gel swelling, swollen gel was extracted from the benzene suspension on a spoon spatula, surface-dried by filter paper, and weighed. The solvent was desorbed by 48 hours' pumping, and the dry weight taken.

The usual definitions of degree of swelling, based on rubber content, were unsuitable for these gels containing large proportions of carbon black. Gel swelling was expressed as the weight of benzene absorbed at equilibrium swelling by 1 gram of the insoluble part of the rubber-carbon black mixture. When no well defined gel was present, as with unmasticated samples, the weight of benzene in the centrifuged deposit was obviously not a true measure of gel swelling. Such weights represented a maximum swelling value, even this being much lower than that for the coherent gels on mastication. Gel swelling measurements were reproducible to only 20 to 30 per cent, as illustrated by the following four repeat determinations of two different workers: 11.0, 11.5, 12.5, and 11.5 and 12.6, 9.4, 12.7 and 10.9. Only trends in gel swelling were considered of significance for comparison with predictions based on gel contents.

The composition of the gels was provided by analysis for free carbon. Dried gels were heated in a combustion tube in a stream of nitrogen. The rubber was thus depolymerized and volatilized to leave free carbon from the carbon black. Philblack O had a content of 98 per cent free carbon and 0.4 per cent ash. The 1.6 per cent adjustment for volatile substances from the carbon black was made on the analysis values to give the carbon black content.

EXPERIMENTAL RESULTS

Milling in air.—Variation of Gel with Extent of Milling.—An unmilled rubber-carbon black mixture gave an opaque suspension in benzene and the sol remained darkened by colloidal carbon black particles after centrifuging. The precipitate was of the same powdery form as that obtained by shaking up carbon black alone in benzene and was more than 80 per cent carbon black. The intrinsic viscosity of the soluble deproteinized crepe remained at its original value (Table I).

TABLE I

GEL PROPERTIES OF DEPROTEINIZED CREPE

(50 p. h. r. Philblack-O mixtures after milling in air)

No. of passes	Gel (%)	Gel swelling (g. benzene/ g gel)	Gel composition (% rubber)	Intrinsic viscosity of soluble rubber
0	33	6	19	5.2
1	49	19	33	4.0
5	64	12	53	2.5
10	65	13	54	2.2
15	64	11	52	—
30	61	10	53	—
100	48	11	38	—
173	37	~4	23	0.5
211	33	~4	27	0.6

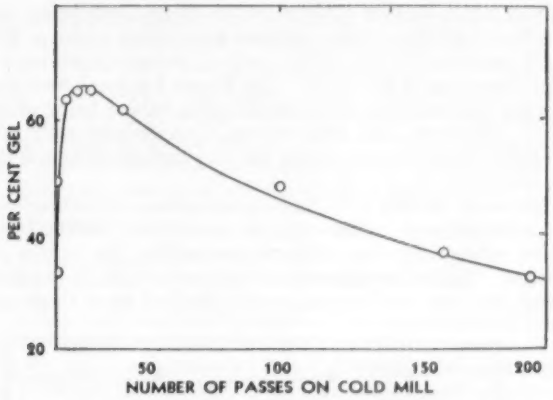


FIG. 1.—Variation of gel content which passes through 0.005-inch nip at roll temperature of 25° C.

Very different dissolution characteristics were noted on one pass through the mill. On suspension in benzene, the liquid remained colorless, while the carbon black was contained in a coherent gel along with a considerable proportion of the rubber. The resistance of the gel to breaking up on shaking increased up to approximately ten passes through the nip. The insoluble material could be dried and reswollen in fresh benzene to the same gel swelling, i.e., it behaved as a rubber network. The sol again darkened slightly after 30 milling passes and, after 100 passes, became opaque and the precipitate reverted to a powdery form.

Gel contents at different extents of milling bear out these qualitative observations (Figure 1), and are supported by gel swellings and composition (Table I).

Variation of Gel with Temperature of Milling.—In contrast to normal thermal reactions, radical production by shear has a negative temperature coefficient[1]. The formation of rubber-carbon black gel also had a negative temperature coefficient (Figure 2). Samples from the same batch of rubber-carbon black mixture were passed five times through the mill at different roll temperatures. Five passes gave gel contents below the maximum and, there-

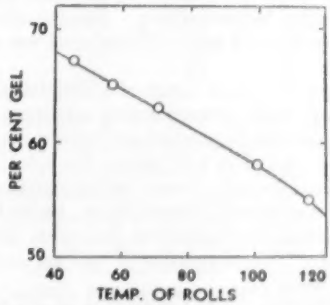


FIG. 2.—Variation of gel content after five passes through 0.005-inch nip, at different temperatures.

fore, no doubt of which portion of the curve of Figure 1 was being investigated. The complication of gel degradation by shear was a minor factor at this extent of milling. As discussed in experimental methods, roll temperatures were of only nominal value; the range of 45° to 115° C of Figure 2 is much overextended, the range of average temperatures of the masticating rubber being of the order of 65° to 90° C. However, the temperature discrepancies only enhance the significant result of direct measurement, viz., that gel production is increased on lowering the temperature.

Gel Formation on Milling with Radical Acceptors.—If rubber-carbon black gel were a manifestation of radical-acceptor reactivity of carbon black, gel content should be reduced by more efficient competition for rubber radicals by added acceptors. Oxygen terminated all ruptured chains on masticating in an internal mixer[1], but may not be comparably effective when these carbon black

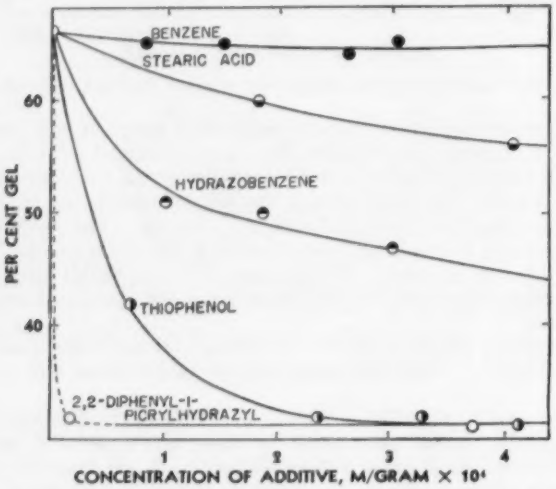


FIG. 3.—Effect of radical acceptors on gel content after five passes through 0.005-inch nip on mill.

dispersions of higher viscosity are milled on an open mill. Therefore, other radical acceptors were added before milling. Nonvolatile solids were dissolved in the benzene solution in the ball mill. Thiophenol was swollen into the dried dispersion.

The radical acceptors, of a wide range of plasticizing efficiency, prevented gel formation on milling, with corresponding efficiency (Figure 3). Visible effects on dissolution properties supported gel content measurements. Instead of a coherent gel and clear sol after five passes, the solutions with as low as 0.5 per cent of efficient radical acceptors were indistinguishable from those of unmasticated mixtures. In sufficient concentration, radical acceptors of different reactivity reduced the insoluble fraction to the value before masticating, and thereafter had no effect. The properties of the gel and viscosity of soluble rubber are recorded in Table II.

An alternative explanation for the reduction in gel by radical acceptors is that they deactivate sites of combination on the surface of the carbon black

particles rather than the sheared rubber chains. This is not supported by pretreatment of the carbon black by radical acceptors, where this mechanism predicts a subsequent reduction in gel on milling (and by later results with Butyl rubber). Philblack-O was pretreated with thiophenol by passing 100 cc. of 1 per cent thiphenol in petroleum ether through a 10-cm. column of black of 1-cm. diameter, washing out the thiophenol with 1 liter of methanol, and drying overnight at a pressure of 10 mm. of mercury at room temperature. The dried Philblack-O gave gel contents on milling equal to those without pretreatment:

Milling passes	0	5	10	15
Gel (%)				
No pretreatment	33	64	65	64
Pretreatment	37	60	66	64

Gel Formation with Different Grades of Carbon Black.—The rate of gel production, the maximum value, and the subsequent decrease of gel content depended on the grade of carbon black. Gel contents at different extents of milling were measured for four carbon blacks of wide use in rubber vulcanizates (Figure 4).

TABLE II

PROPERTIES OF GEL AND SOL VISCOSITY ON ADDITION OF RADICAL ACCEPTORS

Additive	Concn. of additive (moles/g. $\times 10^4$)	Gel			Intrinsic viscosity of soluble rubber
		Gel (%)	Swelling (g. benzene/g. gel)	Rubber (%)	
—	—	66	12	51	1.7
Benzene	0.83	65	11	52	1.8
	1.53	65	11	48	1.5
	2.63	64	11	50	1.7
	3.06	65	13	52	1.8
Stearic acid	1.84	60	13	46	1.4
	4.08	56	14	43	1.7
Hydrazobenzene	0.985	51	14	40	1.5
	1.87	50	14	35	1.9
	3.01	47	13	33	1.8
Thiophenol	0.69	42	8	33	1.45
	2.34	32	3	23	1.4
	3.25	32	3	22	1.2
	4.11	31	3	21	1.15
2,2-Diphenyl-1-picrylhydrazyl	0.16	32	4	34	0.2
	3.71	31	2	20	0.4

Gel with Different Grades of Natural Rubber.—The amount of rubber-carbon black gel, its rate of formation, and its rate of degradation with smoked sheet and extracted pale crepe were similar to results with deproteinized crepe (Figure 5). These rubbers were lightly milled in air to solubilize any macrogel and to reduce the viscosity to that of the deproteinized crepe. The similar gel contents with carbon black dispersed in smoked sheet and deproteinized crepe showed that naturally occurring nonrubber components had no significant effect. The commercial sample of pale crepe gave a much reduced rubber-carbon black gel, and dissolution characteristics resembling unmasticated mixtures. This was plausibly due to xylenethiol or other agent used for bleaching. The

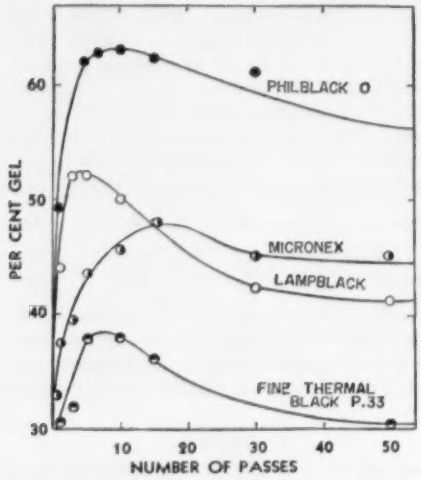


FIG. 4.—Variation of gel content with grade of carbon black.

presence of an efficient radical acceptor was confirmed by normal gel formation after prior acetone extraction of the pale crepe.

The effect of reducing the rubber viscosity was examined with deproteinized crepe. The rubber sample was taken from the stock supply and milled in air to different viscosities as measured in a Wallace plastometer (W.P. units of Figure 5) before the rubber-carbon black dispersion was prepared. Gel contents at the same degree of milling were less than with mixtures containing the unmilled deproteinized crepe.

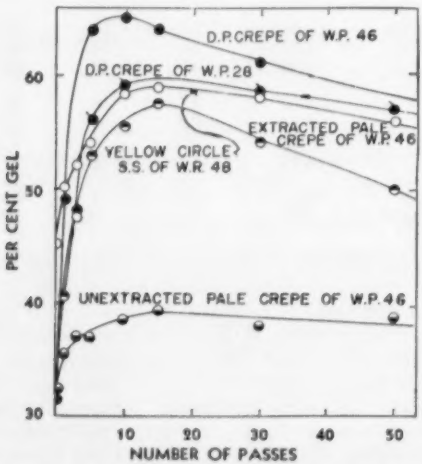


FIG. 5.—Gel content *vs.* degree of milling for different grades of natural rubber.

Gel with Synthetic Elastomers.—The dissolution characteristics of mixtures of carbon black with Neoprene and GR-S were similar to those with natural rubber. With no milling, the mixtures in benzene gave powdery precipitates of carbon black, with only small amounts of adsorbed elastomer and opaque sols. After one pass through a 0.005-inch nip of the open mill, the carbon black and a considerable proportion of the elastomer were bound into a gel, and the sol remained clear. The coherence of the gel increased with further milling. Unlike natural rubber, the solution did not revert to a dark color and the precipitate become powdery on extensive milling. The implied lack of gel degradation is borne out by quantitative measurement of gel content (Figure 6).

Butyl rubber gave no gel on milling (Figure 6), precipitates of carbon black and opaque sols occurring after all stages of milling. This is consistent with the radical hypothesis of gel formation, since Butyl rubber remains unplastiziced on

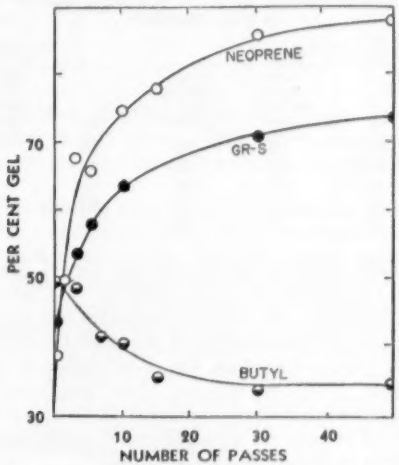


FIG. 6.—Gel production by 50 parts of Philblack-O per 100 of rubber in neoprene, GR-S, and Butyl rubber.

cold milling with radical acceptors. The absence of gel on cold milling when radicals are not produced is more than negative support for the proposed mechanism. It provides a clear demonstration that carbon black is not the active participant in its association with rubber on cold milling, as it is generally supposed to be in its over-all reinforcing action.

Milling in nitrogen.—Comparison with Gel on Milling in Air.—Gel formation by mastication of rubber-carbon black mixtures in nitrogen is greater than that in air at the same extent of mastication (Table III), as anticipated on eliminating the radical acceptor activity of oxygen. The rates of formation of gel are similar up the maximum gel content on masticating in air, occurring in less than 1 minute for the mastications reported in Table III. Thereafter, gel content in nitrogen remains constant for at least 30 minutes of further mastication. Other gel properties on milling in nitrogen are also constant after the initial build-up.

Variation of Milling Temperature.—Equal weights of rubber-carbon black mixtures were masticated for the same period, 15 minutes, in nitrogen at differ-

ent temperatures. The plateau of gel content was attained in this time, and so the results recorded in Table IV are the maximum gel contents on masticating under nitrogen under the shear conditions of the small internal masticator. The maximum gel content and other gel properties were independent of the temperature of milling under nitrogen, while the viscosity of the soluble rubber remained approximately constant at a value much lower than that of the original rubber.

Gel Content on Mastication with Radical Acceptors.—As on milling in air, small additions of radical acceptors modify the production of rubber-carbon black gel on mastication under nitrogen. Radical acceptors which terminate

TABLE III

PROPERTIES OF RUBBER–CARBON BLACK MIXTURES ON MILLING

(3 grams in air and in nitrogen at 30° C in a small internal masticator with a 5-cc. chamber)

	Gel in air			Gel in nitrogen		
Mastication (min.)	%	Swelling (g. benzene/g. gel)	Composition (% rubber)	%	Swelling (g. benzene/g. gel)	Composition (% rubber)
0.33	39	16	39	46	14	43
0.66	44	13	41	48	14	45
5	40	17	38	—	—	—
20	36	18	34	50	10	50
45	33	7	29	46	17	45

sheared rubber chains without cross-linking, e.g., 2,2-diphenyl-1-picrylhydrazyl, also prevent the formation of gel (Table V). Under these shear conditions, intermediate between open mill and internal mixer action, their additional effect on gel production on masticating in the presence of oxygen is undetectable. Cross-linking radical acceptors, e.g., *p*-nitrophenol, do not so effectively reduce gel formation, probably because these compounds form secondary radicals on the sheared rubber chain ends, and these also combine with carbon black. The action of oxygen at atmospheric concentrations effectively suppressed this reactivity of cross-linking acceptors.

DISCUSSION

The nature of the interaction of rubber and carbon black is a long-standing and controversial problem. The various interpretations can be broadly classi-

TABLE IV

PROPERTIES OF RUBBER–CARBON BLACK MIXTURES ON MILLING

(3 grams under nitrogen for 15 minutes at different temperatures in small masticator with a 5-ml. chamber)

	Gel			
Rubber temp. (° C)	%	Swelling (g. benzene/g. gel)	Composition (% rubber)	Intrinsic viscosity of soluble rubber
33	39	14	42	2.2
40	37	13	41	1.9
46.5	35	10	42	2.2
53	39	12	41	2.5
62	32	11	40	2.7

TABLE V

GEL CONTENTS ON MASTICATING 2 GRAMS OF RUBBER–CARBON BLACK MIXTURES WITH RADICAL ACCEPTORS IN AIR AND IN NITROGEN

(At 30° C in small masticator with a 3-cc. chamber)

Additive	Concn. (moles/g. × 10^4)	Mastication (min.)	Gel content (%) In air	Gel content (%) In nitrogen
—	—	1	38	45
—	—	5	41	57
—	—	15	37	55
2,2-Diphenyl-1-picrylhydrazyl	4.00	1	37	38
	—	5	38	39
	—	15	36	37
p-Nitrophenol	4.13	1	34	46
	—	5	38	50
	—	15	38	51

fied as chemical or physical, defining the latter as those not invoking covalent bonding of rubber and carbon black. On balance, physical interpretations of the interaction are favored to explain the various phenomena that have been studied[5].

Experimental data cited in support of proposed mechanisms of interaction have usually been either physical properties of the carbon black particles—in particular, size and adsorptive power—or the elastic behavior of reinforced vulcanizates, or a comparison of the two. The viewpoint adopted here is that more conclusive information on chemical reaction can be gained by direct study of the stages during rubber processing where sufficient energy is supplied to the rubber-carbon black system, i.e., during cold and hot milling and vulcanization. The present discussion is limited to cold milling. Any chemical reactions proceeding must be chemically distinct from those reported on hot milling[6]. Chemical reactivity during vulcanization would appear to await further insight into the vulcanization reactions themselves.

In the absence of carbon black, rubber chains are ruptured by deformation forces during mastication to produce free radicals, probably of the allylic type[1]. It is, then, an obvious starting point to investigate the probable consequences of reaction of these free radicals and carbon black, namely, the prediction of a rubber-carbon black gel. Alternative mechanisms of gel formation must first be considered as operating coincidentally with the established production of free radicals, and, secondly, must explain gel formation and properties under the different experimental conditions chosen for testing the radical hypothesis as rigorously as possible and excluding alternatives.

The strongest evidence for chemical combination is the influence on gel content of substances previously evaluated as radical acceptors[1]. Other modes of action appear unlikely at the low concentrations at which efficient radical acceptors markedly depress gel content (Figure 3). Also, the noncross-linking acceptors of varied chemical type have the same order of efficiency for reducing rubber-carbon black gel and for termination of rubber chains in absence of carbon black. Cross-linking acceptors, on the other hand, do not reduce gel content, as explicable by their producing secondary radicals on the sheared rubber chains.

The combining radical on cold milling in air could be either the allylic, R.,

or the peroxidic, RO_2., readily formed from it with molecular oxygen. That the combining radical is R. is supported by the similarity in rate of gel build-up and maximum gel content in air and in nitrogen, and by the degradation of the rubber-carbon black network on more extensive milling in air by termination of the sheared rubber chains by oxygen. The selective action of *p*-nitrophenol toward R. and RO_2. radicals[1] and its effect on gel content on masticating (Table V) also suggest that R. is the operative radical.

The production and properties of the rubber-carbon black gel on varied conditions can be readily explained by radical reaction. The plateau of gel content after the earliest stages of milling under nitrogen reflects on equilibrium of rates of rubber-carbon black combination and shear of the combined rubber chains, similar to the equilibrium of scission and recombination with rubber alone. This situation is modified on milling in air by the radical-acceptor activity of oxygen. The rapid attaining of a gel maximum not much less than the value under nitrogen is due to the rapid reaction with carbon black. However, once the network reaches a rubber concentration where its rate of rupture compensates for its rate of formation, the superimposed action of oxygen produces degradation. The rubber chains sheared from the network may be the links which bind some of the carbon black into the network, and so a proportion of carbon black passes into the sol fraction. The low intrinsic viscosity of the soluble rubber, the decrease of rubber content and swelling of the gel (Table I), and resistance of the carbon black to centrifuging are consistent with this interpretation.

Different grades of rubber and carbon black give different gel contents under identical milling conditions[7]. The normal nonrubber components are of small influence, but certain rubbers may contain efficient radical acceptors, as is the case with chemically bleached pale crepe. The influence of the rubber itself is primarily that of its molecular weight, gel content increasing with molecular weight (Figure 4). The radical-acceptor efficiency of carbon black should increase with fineness of particle size, structural factors remaining constant, owing to the higher surface area for termination of rubber radicals. This trend is noted with different grades of carbon black. However, structural factors are also important, as revealed by the differences between lampblack and fine thermal black, although of comparable particle size.

The relatively greater effect of carbon blacks on physical properties of GR-S and Neoprene vulcanizates than of natural rubber, and the lesser effect on Butyl rubber under normal processing are coincident with gel formation. GR-S and Neoprene on cold milling form networks with carbon black incorporating most of the elastomer, whereas Butyl rubber gives no network with carbon black (Figure 6). The resistance of these networks to shear degradation is explicable by the low radical-acceptor activity of oxygen with these elastomers compared with natural rubber.

The demonstration of chemical combination of rubber and carbon black during cold milling raises immediately its relevance to the reinforcement of the subsequent vulcanizate. This work has not reached the stage when an answer to this question can be given. Preliminary results indicate that a correlation exists between the reinforcing action of carbon blacks and other fillers (silicates, activated carbonates, whiting, etc.) and the occurrence and amount of gel on cold milling. Also, the properties of the vulcanizate are affected by the extent of milling with carbon black[7]. There appears to be sufficient evidence from gel formation to modify the view currently held that milling is merely a convenient physical method of dispersing the filler.

ACKNOWLEDGMENT

The author greatefully acknowledges the cooperation of R. I. Wood of the technology section, and the experimental assistance of John Davey and Norman Williams. This work is part of the program of research of the British Rubber Producers' Research Association.

REFERENCES

[1] Kolthoff, Gutmacher, and Kahn, *J. Phys. & Colloid Chem.* **55**, 1240 (1951).
[2] Parkinson, *India-Rubber J.* **105**, 976 (1953).
[3] Pike and Watson, *J. Polymer Sci.* **9**, 229 (1952).
[4] Schweitzer, Goodrich, and Burgess, *Rubber Age* (N. Y.) **65**, 651 (1949).
[5] Van den Waarden, *J. Colloid Sci.* **5**, 317 (1950).
[6] Watson, *Proc. 3rd Rubber Technology Conference*, London, **1954**, in press.
[7] Watson and Wilson, *J. Sci. Instruments* **31**, 98 (1954).

DETERMINATION OF THE FATIGUE RESISTANCE OF RUBBER PARTS UNDER CYCLIC SHEAR STRESS IN RELATION TO THEIR SHAPE AND ENERGY *

HERMANN ROELIG AND GUIDO FROMANDI

SCIENTIFIC AND TECHNICAL LABORATORIES, FARBENFABRIKEN BAYER A.G.
LEVERKUSEN, GERMANY

PURPOSE OF THE INVESTIGATION

Rubber is used far less frequently in tension than in compression for spring suspensions and vibration isolation. But for particularly soft springs, it is used in shear. For example, the compression modulus (at a deformation of 10 per cent of the height of the specimen) of a rubber cylinder 25 mm. in diameter and 25 mm. high, of 60° Shore hardness, may be 45 kg. per sq. cm., while its shearing modulus is only 7 kg. per sq. cm. Thus one may obtain a 6.5 times softer spring suspension by a shear mounting for the same volume of rubber. The use of rubber shear suspensions is facilitated by rubber-metal bonds, the quality of which today can be safely controlled technically in rubber factories. Thus we find shear suspensions in rubber-cushioned railway cars and automobile and aircraft construction. The exact design of such spring suspensions still is handicapped by lack of precise data on their fatigue strength, which can be obtained from dynamic tests.

Such information would also facilitate the study of new elastomers and their comparison with those currently in use.

TESTING APPARATUS

Figure 1 shows a photograph of the apparatus; Figure 2 is a schematic diagram, and Figure 3 shows the construction.

Cylindrical metal-rubber specimens of different heights and diameters were tested dynamically in shear. The machine designed for this purpose had to meet the following specifications:

1. The dynamic load (not the amplitude) must be constant and measured and controlled. The usual tests at constant amplitude for the dynamic testing of metals are not very informative for rubber. Rubber specimens flow considerably, relieve the load, and thus give false indications of too favorable fatigue strength under decreasing loads.
2. The bonded surfaces of the specimens must remain parallel, as is so often the case in technical usage.
3. Initial tensile and compression stresses must be applied when necessary. An initial compression stress is particularly frequent in shear springs.

The cylindrical metal-rubber specimens P (see Figure 2) are mounted by their metal end plates in caps K, which revolve freely in ball bearings. The

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 5, No. 10, pages WT 157–161, October 1952. The paper is based on an address at the meeting of the German Rubber Society in Bad Neuenahr, October 13, 1951.

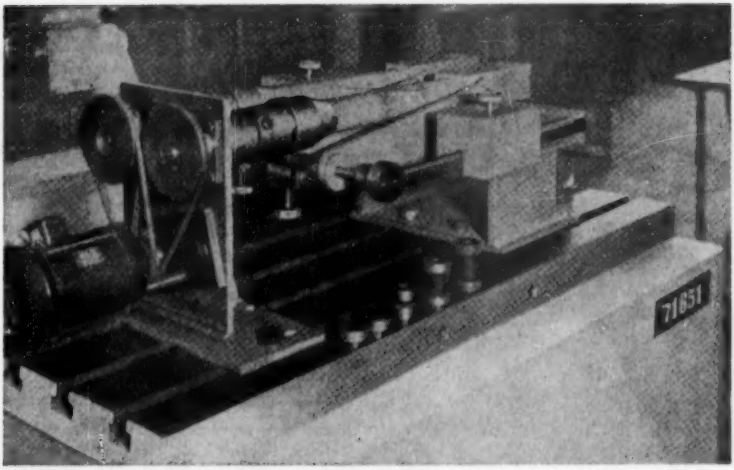


FIG. 1.—Machine assembly for dynamic shear tests of rubber parts composed of elastomers (endurance to dynamic shear).

cap on one end is driven by a V-belt drive A. The device which produces the shearing stress operates on the other end. It consists of a lever system (H_1 and H_2) which serves to transmit the dynamic shear load to the rotating rubber specimen by a static weight G. The shear load can be regulated by means of this movable weight and read on a graduated scale. The lever system is designed so that the end of the lever H_1, on which the specimen is mounted and rotates, describes a large radius (500 mm.) so that the ends of the specimen remain practically parallel, as required. By moving the entire lever arrange-

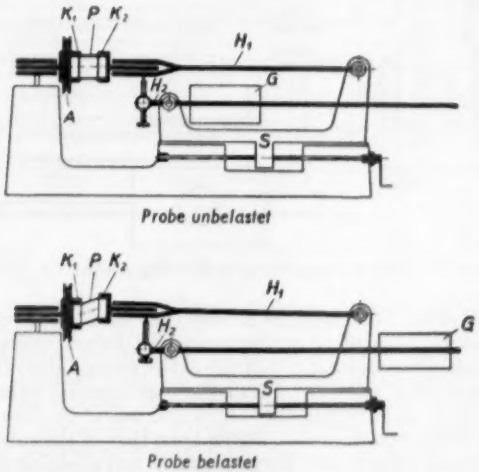


FIG. 2.—Diamgrams of the testing machine for dynamic shear fatigue.

ment on a slide S, a static tensile stress or compression can be imposed on the specimen. Rupture of the specimen is indicated by an electric bell.

EXPERIMENTAL CONDITIONS

It was advisable to use cylindrical metal rubber parts for rotating stress, since the metal-rubber combination provides a convenient mounting. The

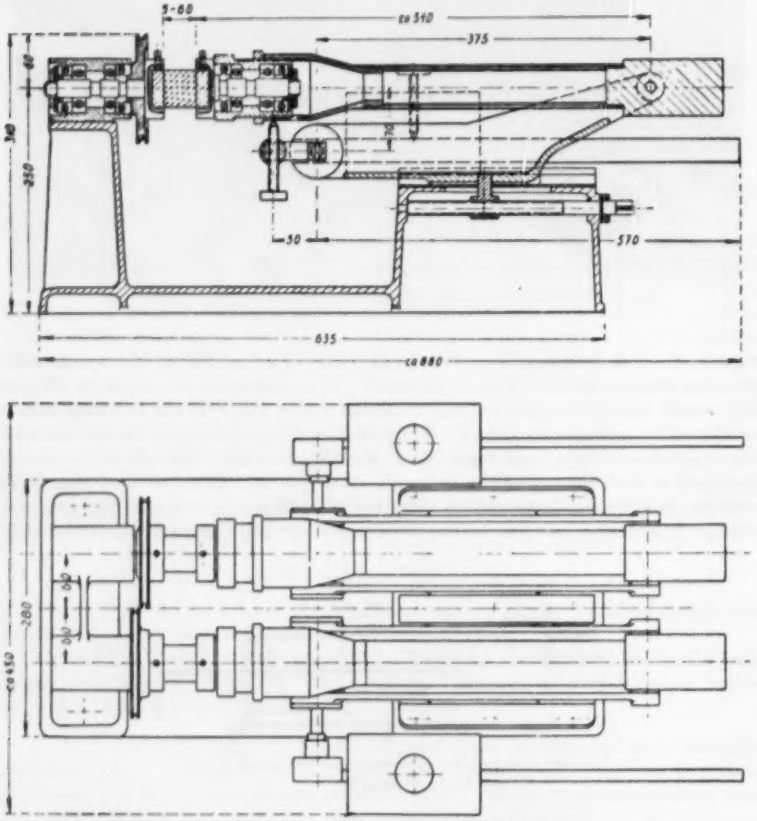


FIG. 3.—Construction of the testing machine.

fatigue strength of the bond must be greater than that of the rubber compound tested. If rupture takes place at the bond, test values under the conditions desired are obtained for this bond, but the entire energy absorption capacity of the rubber is not then utilized. In all the experimental values cited in this study, rupture took place within the rubber and not at the bond. The fatigue strength of the bond was, therefore higher than that of the rubber. A Buna-S solid tire compound (TR 2), 63° Shore hardness and shearing modulus of 9 kg. per sq. cm., was tested first. The test was made at 650 r.p.m. at room tempera-

ture. No great increase of temperature due to damping losses took place during the test.

EXPERIMENTAL RESULTS

The experimental results are first illustrated with the TR-2 compound. Then other compounds, of natural rubber and Buna-S, will be cited for comparison.

TABLE 1

RELATION BETWEEN FORM AND RESISTANCE TO PERIODIC SHEAR

No.	Height h (cm.)	Diameter d (cm.)	Cross-section F (sq. cm.)	Fatigue resistance W_{fe} (kg. per sq. cm.)	h/d	Spring constant $C_f = \frac{S \cdot F^2}{h}$ (kg. per sq. cm.)	Load $P = F \cdot W_{fe}$ (kg.)	Deflection $A = \frac{P}{C}$ (cm.)
1	0.5	1.5	1.77	6.3	0.33	31.85	11.15	0.35
2	1.0	1.5	1.77	4.5	0.67	15.93	7.96	0.50
3	1.0	3.5	9.62	5.4	0.29	86.70	51.90	0.60
4	2.0	1.5	1.77	2.3	1.33	7.97	4.07	0.51
5	2.0	3.5	9.62	3.9	0.57	43.3	37.50	0.87
6	3.0	1.5	1.77	1.8	2.00	5.31	3.18	0.60
7	3.0	2.5	4.91	2.3	14.72	11.29	11.29	0.77
8	3.0	3.5	9.62	2.9	28.90	27.90	27.90	0.96
9	4.0	1.5	1.77	1.6	3.98	2.83	2.83	0.71
10	4.0	2.5	4.91	2.0	14.04	9.82	9.82	0.89
11	4.0	3.5	9.02	2.6	21.67	25.00	25.00	1.15

TABLE 1 (continued)

Energy absorbed $E = \frac{A \cdot P}{2}$ (cmkg.)	Volume $V = F \cdot h$ (cc.)	$\frac{E}{V}$ (cmkg. per cc.)	$\frac{W_{fe}}{d}$	Surface area F_M (sq. cm.)	Form factor $\frac{F}{F_M}$
1.95	0.89	2.20	4.20	2.36	0.753
1.99	1.77	1.12	3.00	4.71	0.376
15.57	9.62	1.62	1.54	11.00	0.875
1.04	3.54	0.29	1.53	9.42	0.188
16.24	19.24	0.84	1.11	22.00	0.437
0.95	5.31	0.18	1.20	14.13	0.125
4.34	14.73	10.29	0.92	23.55	0.208
13.46	28.86	0.47	0.83	33.00	0.291
1.01	7.08	0.14	1.07	18.83	0.094
4.37	19.64	0.22	0.80	31.41	0.156
14.42	38.48	0.37	0.74	44.00	0.219

* s = shear modulus (at 65° Shore hardness; $s = 9$ kg. per sq. cm.).

RELATION BETWEEN SHAPE AND SHEAR FATIGUE STRENGTH

Cylindrical specimens, with different ratios of diameter to height, as is seen in Table 1, were tested.

Specimens of the same dimensions were tested under various specific loads, and the time or number of cycles at which rupture occurred was measured. Finally, a load was reached which was withstood by the particular size and shape of specimen through 6×10^6 load cycles (about 165 hours). If the load thus obtained is plotted as ordinate and the corresponding number of load cycles at rupture as the abscissa, a Wöhler curve is obtained, the asymptote of which gives the fatigue strength of the size tested. Figures 4 and 5 show curves

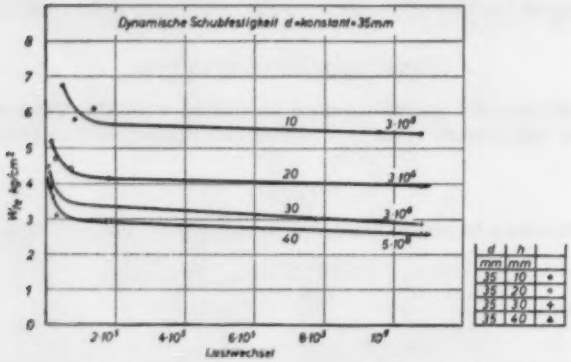


FIG. 4.—Wöhler curves of metal-rubber springs of various dimensions, i.e., constant diameter and different heights. Material TR-2; n = 650 r.p.m. The legend on the diagram refers to the dynamic shear endurance d = constant = 35 mm. The abscissa indicates the periodic load.

of this sort for various sizes, where the diameter remains constant and the height is varied.

It was found that the fatigue strength decreases with increasing height of the specimen, rapidly at first, and then slowly, and approaches a minimum value (see Figure 6). Thus, for example, the resistance of a cylinder 15 mm. in diameter falls from 6.3 kg. per sq. cm. to 1.6 kg. per sq. cm.; that is, to one-quarter, if the height is increased from 5 to 40 mm., that is, eight times.

The softer spring thus has a lower resistance to periodic shearing. These isolated results would be of little practical value, however, if it were not possible to convert them into a generally valid form.

This is possible only if the results obtained refer, not to a single dimension, but to a value which represents the geometrical shape of the specimen. In the rubber literature, the ratio of height to diameter h/d (stiffness) or the form factor F/FM (loaded surface/free surface) has been introduced in derivations of the relations between the shape and spring characteristic of rubber elements.

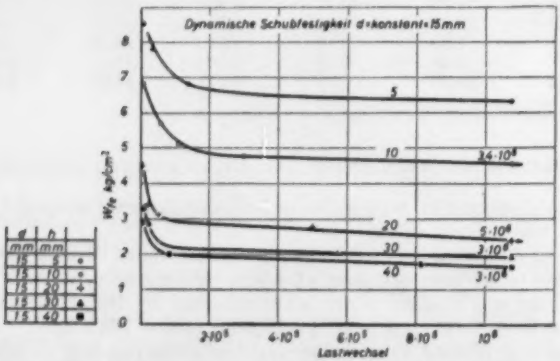


FIG. 5.—Wöhler curves of metal-rubber springs of various dimensions, i.e., constant diameter and different heights. Material TR-2; n = 650 r.p.m. The legend on the diagram refers to the dynamic shear endurance d = constant = 35 mm. The abscissa indicates the periodic load.

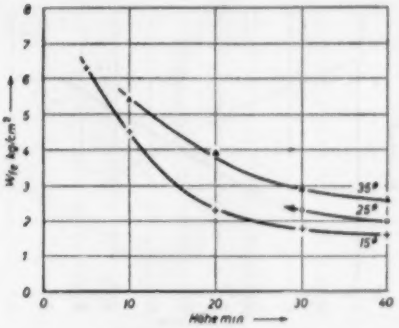


FIG. 6.—Fatigue endurance and dimensions (TR-2). The abscissa indicates the height in mm.

If the measured fatigue strength of the specimens is plotted against h/d, a clearly defined dependence of fatigue strength on h/d is obtained, as shown in Figure 7. The points for all the rubber pieces tested lie on the same curve. This curve characterizes the dynamic relations of the rubber compound tested in a more general way for all the elastomers tested. Analogously, a well defined relation between fatigue strength and the form factor is also obtained (Figure 8). Thus, if the dimensions of a rubber spring are calculated for the spring properties, one can determine from the relation just derived how heavily this rubber spring can be dynamically loaded. It is found that relatively soft springs (high h/d ratio or low form factor) cannot withstand anywhere nearly so high dynamic loads as can harder ones. This is explained by the greater amplitude of the softer springs under the same load. Soft springs have a higher energy absorption under the same load.

RELATION BETWEEN SPECIFIC ABSORPTION OF ENERGY AND FATIGUE STRENGTH

Whether made of steel, rubber, or any other material, a characteristic property of springs is their capacity to store energy. This capacity for absorbing energy can be expressed in mkg. per cc. of the material. The fatigue strength

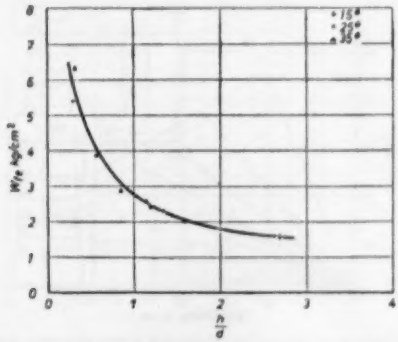


FIG. 7.—Fatigue endurance and stiffness (TR-2).

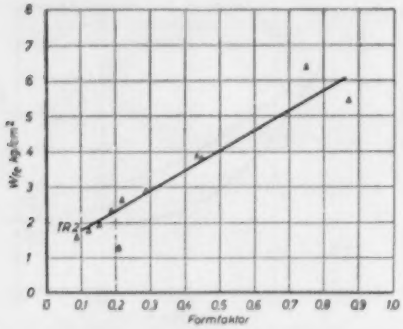


FIG. 8.—Fatigue resistance vs. f (form factor) (TR 2). The abscissa indicates the form factor.

obtained from the measurements illustrated makes it possible to derive the maximum possible energy absorption of a spring from the stress-strain diagram (the spring characteristic) of the rubber compound tested. This is obtained from the area of the right-angled triangle whose ordinate represents the force corresponding to the fatigue strength and whose abscissa is the deformation corresponding to this load. The slope of the stress-strain diagram (Figure 9) corresponds to the spring constant in kg. per cm. The energy absorption E per unit volume of rubber spring stands in simple relation to the fatigue strength and the shear modulus, which are both known. This relation is expressed thus:

$$\frac{E}{V} = \frac{W_{fe}^2}{2s}$$

Here E is the energy absorption of the spring in cmkg., V is the volume of the spring in cc., W_{fe} is the fatigue strength of the rubber mixture in kg. per sq. cm., and s is the shear modulus in kg. per sq. cm.

Here s is calculated from the relation:

$$s = \frac{C \cdot h}{F}$$

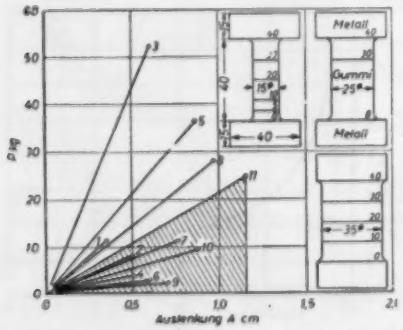


FIG. 9.—Fatigue resistance and spring diagram (material TR 2). The rubber test-specimen lies between the two metal caps. The abscissa indicates the deflection A in cm.

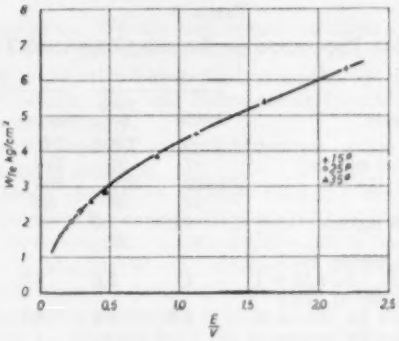


FIG. 10.—Fatigue resistance and specific power consumed (material TR 2).

where C is the spring constant of the cylindrical spring in kg. per cm., h is the height of the cylinder in cm., and F is the cross-section of the cylinder in sq. cm.

Again there is a simple relation between this specific energy absorption and the fatigue strength (Figure 10). The curve which includes the values for all the cylindrical springs tested characterizes the compound tested (TR-2). It can be seen from this curve that, for soft springs, 1 cc. of rubber can withstand 0.25 to 0.5 cmkg. dynamically; and that this specific energy absorption can be raised in hard springs to over 2 cmkg. per cc. of rubber.

EXPERIMENTAL RESULTS FOR OTHER RUBBER COMPOUNDS

The measurements made on the Buna-S tire compound were repeated on other rubber compounds. Natural rubber also was included in the studies. Since the fundamental course of the characteristic curves: Fatigue strength vs. f (form factor), and Fatigue strength vs. f (specific energy absorption), is known, it is possible to limit one's self to obtaining three Wöhler curves for three form factors which differ as widely as possible in testing other compounds.

In addition to the Buna-S solid tire compound, four other compounds were tested: a Buna-S spring compound; a natural-rubber tire-tread compound; a

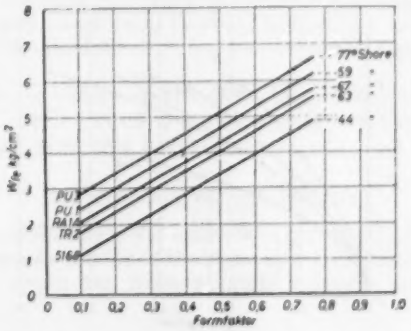


FIG. 11.—Fatigue resistance vs. f (form factor) of various rubber compounds. The abscissa indicates the form factor.

TABLE 2

TECHNICAL PROPERTIES OF RUBBER COMPOUNDS TESTED

Type of product	Buna-S		Natural rubber		
	Spring	Solid tire	Carcass	Solid tire	Spring
Type no.	5168	TR 2	PU 1	RA 1B	PU 3
Tensile strength (kg. per sq. cm.)	67	92	210	175	140
Elongation at rupture (%)	510	370	565	430	380
Hardness (° Shore)	44	63	59	67	77
Shear modulus (kg. per sq. cm.)	5.0	9.0	8	13	25
Damping (%)	18	20	5	14	13
Fatigue resistance (kg. per sq. cm.) for form factor 0.25, 1.3., $h/d = 1$	2	2.6	3.3	2.9	3.7
Fatigue resistance (kg. per sq. cm.) for form factor 0.75, i.e., $h/d = 3$	4.8	5.4	6.1	5.7	6.6
Specific power consumed for fatigue resistance of 4 kg. per sq. cm.	1.7	0.9	0.9	0.7	0.5

natural-rubber carcass compound, and a natural-rubber spring compound. Figures 11 and 12 show the characteristic curves. Table 2 gives the technical data for the compounds.

It is seen that the fatigue strength for the various compounds increases practically linearly with the form factor (Figure 11). The three natural-rubber compounds show higher fatigue strengths than do the two Buna-S compounds. This difference will probably not be overrated, if the differences of hardness are taken into account (see Table 2). It can be assumed that the energy absorbed is proportional to the work of destruction leading to rupture. Figure 11 confirms that the fatigue strength decreases with decrease of the form factor, while thinner softer specimens absorb more energy under the same load. For the same reason, however, the softer compound also absorbs more energy than the harder one when the specimens are of the same size, and the softer compound will have a lower fatigue strength, assuming, of course, that the proportion of the work of destruction which is contained in the energy absorption is the same for both (Figure 13, upper left). One can assume that this work of destruction is proportional to the damping loss, and this latter does not vary greatly in four of the five compounds tested. On the contrary, the fifth, the natural-rubber carcass compound, contrasts favorably, despite its low hardness, be-

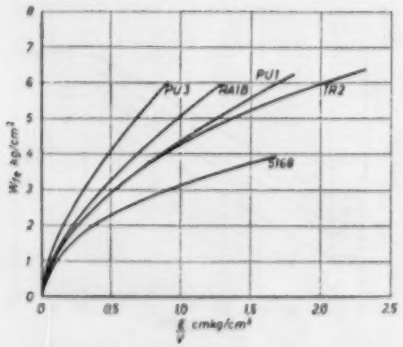


FIG. 12.—Fatigue resistance and specific power consumption of various rubber compounds.

cause of its low damping. We can thus regard hardness (and accordingly the shear modulus), as well as damping, as factors which determine fatigue strength. It would be worthwhile to extend these studies to other types of compounds, and particularly to Perbunan. The tear resistance and impact resistance offer no criterion of the fatigue strength.

Figure 12 shows the specific energy absorption of the various compounds in relation to the fatigue strength.

The specific energy absorption extends from 0.5 to 2 cmkg. per cc. for current sizes, and thus is of the same order of magnitude as that for steel springs.

In conclusion, the assumption on which this study is based should be stated again, i.e., that the Wöhler curves were obtained for a constant force amplitude, Figure 13 shows that, when the damping loops 1 and 2 are compared at constant force amplitude, the harder compound is more favorably situated (loop 2) than the softer one (loop 1), because both the energy absorption and (with equal

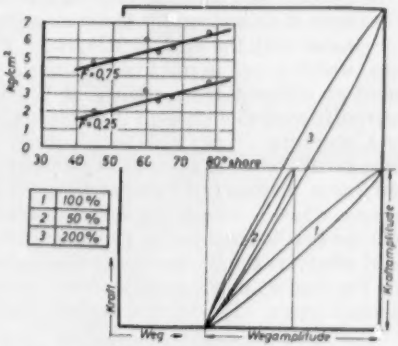


FIG. 13.—Damping losses with constant power and with constant deformation. The lower left abscissa is the displacement; the lower right abscissa is the amplitude of displacement; the lower left ordinate is the power; the lower right ordinate is the amplitude of the power applied.

damping) the absolute loss of energy per deformation cycle are lower for the harder of the two dynamically stressed rubber compounds. If the experiments had been made at constant amplitude, the relation would have been reversed; that is, the softer compound (loop 1) would have shown the lower energy absorption and smaller absolute damping loss in comparison with the harder compound (loop 3).

The study could, to be sure, be broadened by including an initial stress and a precompression. Such a series of experiments is now being carried on, and they will be reported when they are concluded.

REPRESENTATIVE APPLICATIONS

The present investigation is the outcome of considerations of sheared tires, and the test corresponds exactly to the stress in a cylindrical section cut out of such a tire. The results are, however, quite generally applicable to shear-springs.

NEW INSTRUMENTS FOR MEASURING HARDNESS *

STEFANO OBERTO

RESEARCH AND DEVELOPMENT LABORATORIES, PIRELLI SOCIETÀ PER AZIONI, MILAN, ITALY

In the Pirelli laboratories, hardness measurements of vulcanized rubber have always been the subject of considerable attention, not only from the viewpoint of making such a test in accordance with carefully developed standards, but also from the long range viewpoint of designing and constructing instruments better adapted for the purpose and more precise than those available at the time. The earliest example of an instrument based on an original concept appeared in 1923 and originated with the work of Marzetti. Figure 1 is a general view of the apparatus, which is still in use for some work. As a test method which can be operated at different temperatures, it had unquestionable advantages over commercially available types of instruments, and it has retained these advantages for a long time.

The indentor of the Pirelli durometer, as the instrument has been termed, is a cylindrical point, of 2 mm. diameter, with a flat base. This point sinks into the rubber test-specimen, which is usually the center disk left after a Schopper ring has been died out for tensile tests on the dynamometer. The disk is generally 4 mm. thick, but whatever the thickness and source, the disk should have plane parallel faces. The load is applied on the point by a lever, and consists of weights resting on a balance pan. Readings of the indentation are made by an optical method.

The specific feature of the Pirelli hardness test is to determine the load, in grams, which makes the point sink into the rubber exactly 1 mm. in 15 seconds of application, starting from a "zero" position defined by an initial load of 100 grams. To establish this, several trials are necessary, and therefore the measurement is not immediate. The time for the test can be reduced by using two loads, one of which gives a slightly larger indentation than 1 mm. and the other of which gives a slightly smaller indentation, and interpolating the load required for 1 mm. indentation between these two loads. The load-indentation interpolation is linear with the cylindrical point, as both theory and experiment demonstrate.

Since the same instrument can be operated quite satisfactorily with a constant load, and reading of the resulting indentation, the choice of the somewhat more laborious procedure of constant depth had to show at least one reason for its use. The reason is that it gives increasing values with increase of hardness as would be judged by sensory methods, and because it is then possible to obtain uniform measurements, with the same sensitivity both for soft rubber and for hard rubber, since the influence of the thickness of the test-specimen is minimized. The Defo hardness test for raw natural rubber and synthetic rubbers is based on the same principle, and, among durometers, the ICI apparatus[1] likewise applies the principle of testing at constant deformation, but

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Pirelli Ricerca e Sviluppo*, No. 2, pages 1–20, October 1954.

avoids the making of successive tests with a different method of applying and measuring the load.

The cylindrical point of 2 mm. diameter used in the Pirelli durometer has, then, been retained in the standardizing of hardness testing[2] in Italy, but in the standardized test it was desired at the time to avoid the making of successive trials with different weights, as the original Pirelli durometer was operated. Based on the linear relation between load and depth of indentation of the cylindrical point, the use of three loads decidedly different (400, 1000, and 2500

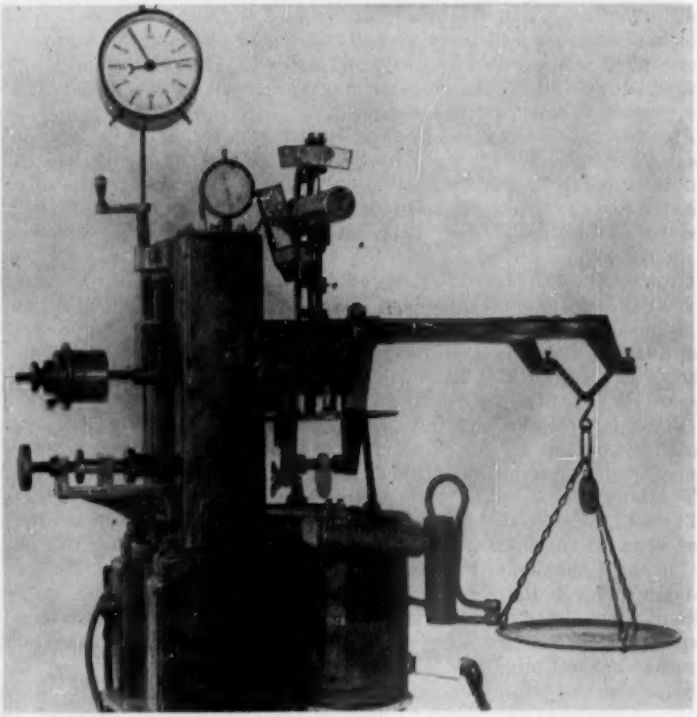


FIG. 1.—Durometer developed in the Pirelli laboratories by Marzetti in 1923. The sample to be tested, in the form of a disk, is placed vertically between a cylindrical point and a small base at the center. The load acting through the point is applied as weights on the balance pan. Normally the measurement is made by trial to determine what load gives a depth of indentation of the point of one millimeter. With this durometer, measurements can be made at different temperatures by raising the lower tank.

grams) has been chosen as satisfactory for measurements which involve depths of indentation of the test-specimen between 0.5 and 1.5 mm., and the load per mm. of indentation is then calculated.

The representation of hardness in terms of UNI "hardness indexes" has not found great favor in Italy; similarly the individual national standards have not always received favorable receptions in the various countries, all of which standards are characterized by the constant load method (the Italian standard is the sole exception), but at the same time different loads, different dimensions of the indentor, and different ways of expressing the results are used. Apart

from the truly international use of the Shore-A durometer degrees, the other durometer scales, official and unofficial, have been related to one another by numerical tables or by nomograms, derived from comparative experimental data which are more or less reliable.

As the use of the Shore A durometer and corresponding units continued to become more and more extensive, and as greater demands on the sensitivity, precision, and reproducibility were often being made on pocket instruments than could be expected of them, numerous cases of disagreement were verified on account of discordant readings made with different instruments. The Pirelli laboratories therefore made a new and thorough examination of the problem of hardness measurements. The purpose was to develop a method of measurement which would be easily adaptable for general use and an instrument which would have the precision and reproducibility of results which were indispensable to the growing demands.

An examination of the most recent literature on the subject showed in particular the extensive work done by Scott and others[3] at the British Rubber Manufacturers' Research Association on the measurement of hardness, on the basis of which the British standard for measuring hardness was established, and presented at the ISO/TC 45 in 1948, with the proposal that it be introduced as the international standard.

Even on first examination, the procedure introduced by Scott showed itself to be an interesting one, capable of giving to the measurement of hardness a definite physical meaning and, above all, capable, as a numerical representation of hardness, of being adapted for general use with a minimum of difficulty in different countries. The likelihood, therefore, of seeing such a procedure accepted in the not too distant future as an international standard has prompted the Pirelli laboratories to study without delay what instrument capable of measuring hardness by the Scott method would have, at the same time, the sensitivity and reproducibility which appeared so indispensable.

The work carried out in the laboratories at Bicocca, while approaching the goal desired, has also served for studying in detail the features of the test proposed as an international standard method and has lent support to the proposal itself in the discussion of the ISO/TC 45. As things now stand, the proposal is about to reach the status of ISO Recommendation, and the use of the method, while already current in Britain and its Dominions, has been widely accepted in all of Western Europe, and its acceptance in the near future by those concerned in the United States of America seems at least possible.

Since this test will probably become a part of the Italian standardization, it may be useful at this point to describe the experimental procedure before introducing the instrument which has appeared to be best adapted to the carrying out of the test.

The measurement of hardness, according to the ISO Recommendation comprises: (1) measuring the change of indentation of a vulcanizate by a sphere, of 2.44 ($\pm$ 0.06) mm. diameter, when the load which is applied perpendicularly to the original surface is increased from 30 to 570 ($\pm$ 5) grams; the final reading is measured 30 seconds after application of the maximum load; and (2) converting, by means of a graph or table derived from a definite formula, the measurement of the indentation into an index or degree of hardness.

It is understood that the temperature of testing is normally 20° C, and that the test-specimen is cut from a sheet with plane parallel surfaces 8–10 mm. distant and with lateral dimensions at least 8 times the thickness. The depth of indentation of the sphere is measured relative to the upper face of the test-

specimen, on which rests, to define the position, a foot having a plane surface of circular form, an outside diameter of 20 mm., an inside diameter of 5 mm., and which is loaded by a weight of 250 grams per sq. cm. (see Figure 2). This foot has been designated by us as a "piede anulare" (annular foot) as a free translation of "presser foot" and "pied presseur", with a view to defining it by its form rather than by its function, which is not primarily that of applying

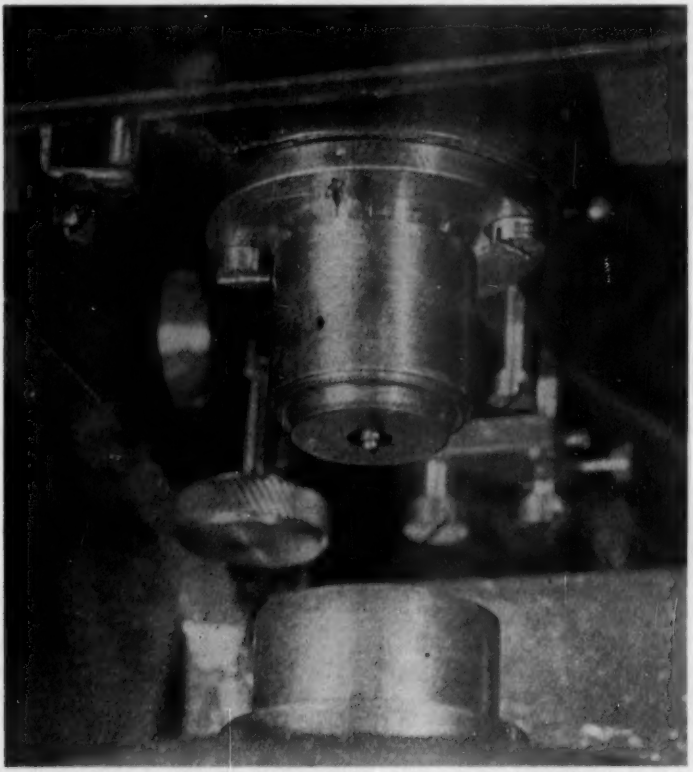


FIG. 2.—Detailed view of the annular foot of a durometer constructed in the Pirelli laboratories in accordance with the ISO specifications, although not in the more recent edition. The indentor with ball point protrudes from the center opening. The lower smooth surface of the annular foot rests on the upper face of the test-specimen, which is on the cylindrical platform below. The position of the ball is measured with reference to the annular foot.

pressure. All pocket durometers have annular feet. It is, of course, understood that the indentor is at the exact center of the opening.

The annular foot is employed so that the measurement of the indentation does not depend on the deformations of the instrument, and to ensure the test-specimen, which eventually because of internal stresses shows a slight concavity on the lower face, is in contact with the base throughout the test.

To recapitulate: the test-specimen is supported on the base of the instrument; the annular foot is lowered onto the test-specimen, together with the point loaded with thirty grams; at the end of five seconds the position of the

indentor with respect to the annular foot is read on a scale; a supplementary weight of 540 grams is applied to the point, and after 30 seconds the position of the point is read on the scale. The first reading can be replaced by making the scale read zero; in any case, a difference of readings, or a reading, L is obtained, which represents the change of depth of indentation relative to the two loads.

A noteworthy feature is that the loads applied to the point are actually those indicated. Some types of micrometer have in their mechanism an opposing spring which acts on the point in a variable way by frictional effects and with different effects according to the readings. To reduce the influence of these frictional phenomena when present, it is recommended that the instrument be vibrated slightly before making a reading. However, the load contributed by the micrometer should be determined specifically.

Even with all this attention to precision of technique, the operation is still not truly defined; for example, the application of 540 grams must be gradual, without impact, but on the other hand, the load must not be applied too slowly if the 30 seconds' delay in measuring is to have any significance.

In view of all this, the testing procedure becomes a truly classic procedure, so much so, in fact, that it might be asked why the loads which have been chosen are not simpler or in round numbers. As a general answer to this, it can be said that the intention was to obtain a difference of depths of identation of 1 mm. for a rubber mixture of average hardness, represented as the value of 50 in terms of Shore A hardness. Then if one wishes, quite justifiably, not to use large loads and also avoid having the ball sink into the softest rubbers met in practice to a depth greater than the diameter of the ball, it must be decided first what should be the diameter of the ball just above 2 mm. (decided on the basis of balls currently manufactured) and, second, the load to be used with that particular size of ball.

The choice of the sperical form of indentor is the result first of all of the availability of metal balls which fulfill all the desired requisites of precision and uniformity. Scott himself took into consideration the use of cylindrical and conical forms of indentors, but the difficulties of defining their corner edges and the ease with which these edges might be damaged in service are arguments against their general use.

The procedure is quite classic, let us say, up to the point when the depth of indentation of the indentor is measured or, rather, the increase of indentation. So true is this that the British hardness was, and also the American is, expressed directly, with a certain degree of contradiction, by the value of the depth of indentation.

It is in this second respect that the method of measuring hardness proposed by Scott differs from all preceding methods. Scott starts from the concept that the deformation of a rubber sample caused by an indentor is a function of the modulus of elasticity of the rubber, at least if one is prepared to speak of one modulus, independent of the after-elastic effects which are present to some extent in high polymers in general and in vulcanized rubbers in particular.

In view of the constancy of volume of rubber during deformation, and again reasoning in accord with the principles of small deformations, the modulus of elasticity resolves itself into the shear modulus. In the particular case of an indentor of spherical form, and based on considerations of dimensions of the units and experimental results, Scott derived the following relation:

$$P = 0.00051 \cdot G.R.^{0.65} \cdot H^{1.25}$$

where P is the load in kg. applied to the indentor, G is the shear modulus in kg. per sq. cm., R is the radius of the indentor in cm., and H is the depth of indentation in hundredths of a mm. A relation not much different for the exponential values is obtained by starting from the formulas of Hertz on the approach of two elastic spheres which press against each other. Schreuer[4] has recently studied this problem, and some interesting experiments on the subject have likewise been made in the Pirelli laboratories (see Figure 3).

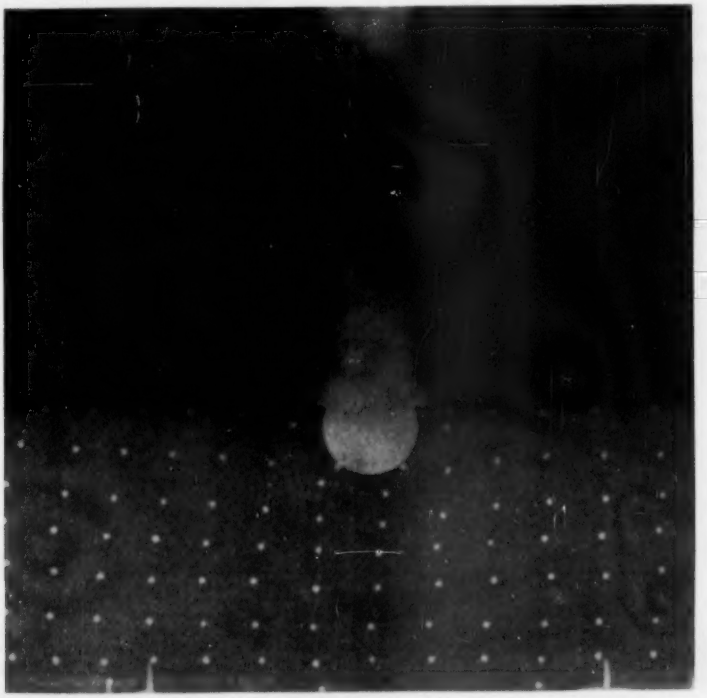


FIG. 3.—Radiograph of a piece of vulcanized rubber in whose middle section lead shot has been placed at more or less regular intervals. A ball has penetrated into the rubber. This radiograph was taken in the Pirelli laboratories in connection with an investigation of the internal deformations in rubber during a hardness measurement, with the idea of comparing the distribution of the displacements with those predicted by the theory of elasticity.

Hence measurement of the hardness of rubber is actually a measurement of the shear modulus of the material, though a static modulus, and the final hardness measurement would be this same shear modulus.

The representation of hardness (a parameter which has always been empirical) in terms of the modulus, which is a physical constant of evident significance and from which, in principle, the forces in all deformations of rubber can be determined, has been appreciated in the Pirelli laboratories. For several years we were instructed to use definite physical parameters instead of the more classic methods of rubber technology, which are often too closely related to some particular method of testing or to some particular apparatus. Moreover,

the Pirelli hardness values as determined with the durometer constructed by Dr. Marzetti, as a measure of the elastic reaction for a constant indentation, were practically proportional to the shear moduli of different materials; all the measurements made in the past gave, with a proportionality factor, both the shear moduli and the moduli now obtained with ball indentor.

Nevertheless, Scott has maintained that the final representation of the test result does not necessarily have to be the shear modulus. The shear modulus is not or, it might be said, is not yet generally used, and its introduction as an index of hardness might encounter a certain resistance. Moreover, hardness when regarded as a sensory phenomenon (e.g., the reaction of a rubber product to the finger nail) should increase with the logarithm of the physical value in ques-

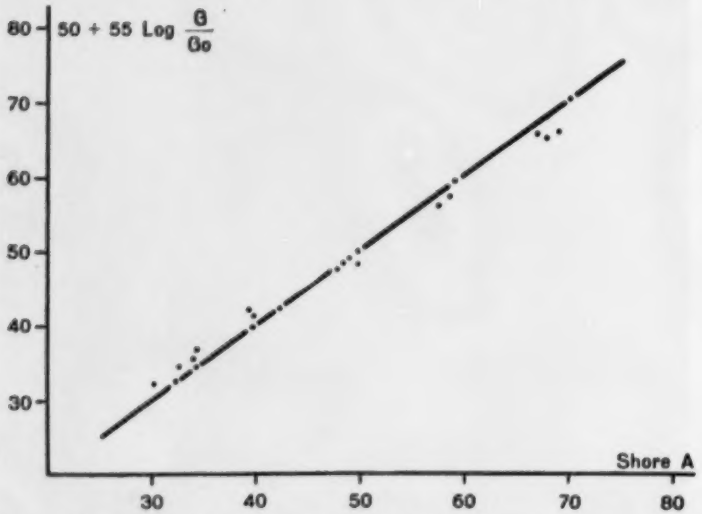


FIG. 4.—The abscissa represents the values of the Shore A hardness of a series of vulcanizates of natural rubber. The ordinate represents the values of the expression: $50 + 55 \log (G/G_0)$, where G_0 is the shear modulus of vulcanizates having Shore hardness of 50. The relation is practically linear in the range considered.

tion (the reaction itself). Now the Shore A hardness scale, so widely used and so well established in all branches of rubber technology, shows, when plotted as a function of the logarithm of the modulus of natural-rubber vulcanizates, precisely a straight line in the middle of the scale (see Figure 4). Scott has attempted to derive a mathematical function of the modulus such that it would be 0 and 100, respectively, for very low and very high moduli, and would be proportional to the logarithm of the modulus within certain limits.

Possessing a function of this kind, it is possible practically to parallel the Shore scale by the shear modulus, i.e., it is possible to set up a hardness scale practically coincident with the Shore scale, although derived quite independently. No difficulty is encountered on practical grounds in the introduction of a scale of this kind because it does not displace or replace any personal experience and sensory impression already established.

The function adapted to the purpose is the following:

$$f = \frac{100}{\sigma\sqrt{\pi}} \int_{-\infty}^{\log(G/G_0)} \cdot e^{-x^2/\sigma^2}\, dx \quad \text{with} \quad \sigma = \frac{100}{\alpha\sqrt{\pi}}$$

where α is the slope of the Shore curve with respect to the logarithm of the modulus at the center of the scale, numerically equal to 54 (54 Shore units for a ten-fold increase of the modulus) and G_0, the modulus of rigidity at the center of the scale, is 7.4 kg. per sq. cm. The logarithms shown here are decimal logarithms.

This function f is zero for zero modulus, is 100 for infinitely high modulus, and is 50 for a modulus of 7.4 kg. per sq. cm., which corresponds to 50 Shore hardness. The slope of the curve with respect to the logarithm of G, when G is 7.4, is exactly α, the slope of the Shore hardness curve. The Shore and f scale practically coincide between 30 and 80 Shore values, with small differences outside of this range, and again with coincidence at the upper limit, while at the lower limit a small difference remains because zero Shore represents a rubber of finite modulus.

Various other expressions are equivalent to the preceding one.

$$\frac{100}{\sqrt{\pi}} \int_{-\infty}^{(1/\sigma).\log(G/G_0)} \cdot e^{-y^2} dy \qquad \frac{100}{\sqrt{\pi}} \int_{-\infty}^{0.957\log(G/7.4)} \cdot e^{-y^2} dy$$

(A) $$\frac{100}{\sqrt{\pi}} \int_{-\infty}^{0.957\log G - 0.827} \cdot e^{-y^2} dy$$

(B) $$\frac{100}{\sqrt{2}\cdot\sqrt{\pi}} \int_{-\infty}^{1.35\log G - 1.160} \cdot e^{-y^2/2} dy$$

(C) $$\frac{100}{\sqrt{2}\cdot\sqrt{\pi}} \int_{-\infty}^{1.35\log G + 3.840 - 5} \cdot e^{y^2/2} dy$$

There can be found, particularly in treatises on statistics, tables which give the values of the expressions (A) and (B) as a function of the upper limit of the integral and similarly of (C) in which the final figure of 5 is omitted (Probit tables).

The conversion from the readings of the depth of indentation by the durometer to the hardness values is not made, however, by calculation of the moduli of rigidity G and then by calculation of one of the integrals recorded. A simple table makes it possible to read directly the final values, which will be known under the name of International Rubber Hardness Degrees (IRHD).

For convenience, Table I gives these values, with only two significant digits planned for ordinary usage.

It should be noted that the tables gives the differences of the depth of indentation of the 2.44 mm. diameter ball corresponding to loads of 30 and 570 grams, differences which are designated by L. Calculation of the modulus must take into account the complete indentation of the point, from the unstrained surface. This is indicated by H. For definite loads, like those which are concerned here, it is possible. when L is known, to calculate H. From the

formula of Scott, there is obtained:

$$H_{570} = \frac{L}{1 - \left(\frac{30}{570}\right)^{0.74}} = \frac{L}{1 - 0.113} = 1.13L$$

Hence, the depth of indentation of the ball under a load of 30 grams, the initial load, contact load, or "zero" load, is of the order of 10 per cent of the depth of indentation under the final load. This information is not used in practice, but it does give an idea of the amount of the correction for setting at zero reading the instruments which require it, and also an idea of the notable influence which an uncertain initial load can have on the first reading.

Coming now to the designing by the Pirelli laboratories of an instrument particularly adapted to the measurement of the International Rubber Hardness Degrees, a plan which has been completed by the construction of several prototypes, it should be emphasized that the attempt has been made to obtain a particularly simple operation, sturdiness, and high degree of precision.

At the present time, we are still not prepared to pass judgment on tests made with several instruments in several places, but the results obtained by various operators, with the instrument constructed in the workshop of the Pirelli laboratories (see Figure 5), partly from current work and partly from planned experiments with statistical analysis of the results, make it possible to describe the instrument with some confidence as to its success.

For the indentor, only 2.36 mm. diameter balls were available, so at the

TABLE 1

RELATION BETWEEN THE DIFFERENCE L OF READINGS WITH THE PIRELLI INSTRUMENT AND INTERNATIONAL RUBBER HARDNESS DEGREES

TABLE 1

L	0	1	2	3	4	5	6	7	8	9
0	100	100	100	100	99	99	99	98	98	97
10	97	96	95	95	94	93	93	92	92	91
20	90	89	89	88	87	86	86	85	84	84
30	83	82	82	81	80	80	79	78	78	77
40	77	76	75	75	74	74	73	73	72	71
50	71	70	70	69	69	68	68	67	67	66
60	66	65	65	64	64	63	63	62	62	62
70	61	61	60	60	59	59	59	58	58	57
80	57	57	56	56	56	55	55	54	54	54
90	53	53	53	52	52	52	51	51	51	50
100	50	50	49	49	49	48	48	48	48	47
110	47	47	46	46	46	46	45	45	45	45
120	44	44	44	43	43	43	43	42	42	42
130	42	42	41	41	41	41	40	40	40	40
140	40	39	39	39	39	38	38	38	38	38
150	37	37	37	37	37	36	36	36	36	36
160	35	35	35	35	35	35	34	34	34	34
170	34	34	34	33	33	33	33	33	33	33
180	33	32	32	32	32	32	32	32	32	31
190	31	31	31	31	31	31	31	31	31	31
200	30	30	30	30	30	30	30	30	30	30

With this table, which is derived from the English Standards, it is possible to obtain, by starting from the increment of depth of indentation by application of an increased load, the values of hardness in International Degrees.

For example, L = 116 mm./100 IRHD 45.

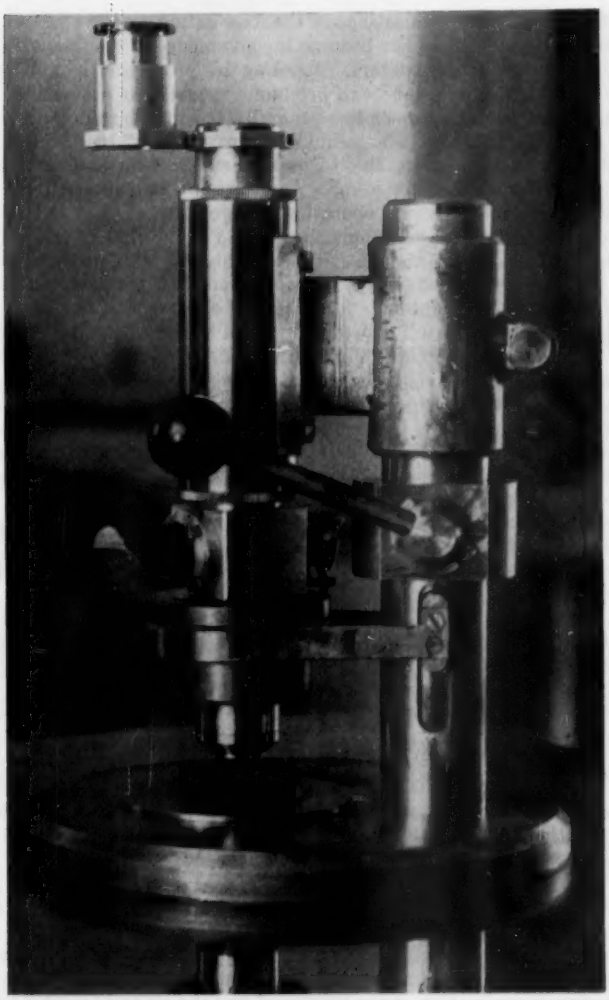


FIG. 5.—Durometer constructed in the workshop of the Pirelli laboratories in accordance with the ISO recommendations for the measurement of hardness, and with which tests have been carried on for two years for the purpose of ascertaining the practicability and precision of the instrument.

lower tolerance limit of ISO recommendation, this figure was accepted and, correspondingly, the load increase of 535 grams was also used.

An optical method of measurement was chosen for the depth of indentation, with a micrometer objective (2 mm. divided into 200 parts) attached to the stem of the indentor. The objective was 10 × and the eye-piece with crossed reticule 10 ×, both attached to the tube which terminates in the annular foot.

The reason for optical readings is to avoid practically all friction and any

spring effect apt to cause variations of the load acting on the ball, particularly in the first reading. There has been no inconvenience in reading with the eyepiece by numerous experimenters. Reading by projection would have been adopted later, had there not been economic reasons to prevent it, i.e., the apparatus would then have been less generally acceptable to prospective users.

It is advisable to make two readings, one with "zero" load, the other with the total load; i.e., it is preferable to make a subtraction to a setting at zero reading of the scale, thus avoiding a complication in the construction and, above all, not wishing, with an operation of zero setting, to have the operator get the idea that the depth of indentation is zero at the time of the initial reading. The instrument can, though not necessarily, be tared in such a way that the first reading corresponds, for a test-specimen with perfectly plane parallel faces, to the depth of indentation under a load of 30 grams.

Readings can be made without difficulty to a hundredth of a millimeter, and a half or a third of this fraction can be estimated. This is, however, absolutely superfluous in measuring the hardness of rubber, but it may be useful either when the material being tested is a rather hard plastic or when, in measuring the hardness of a material, it is desired to read at the same time the residual deformation of the vulcanizate, removing the principal load after measuring the hardness, and leaving the contact load to act naturally. Here too, the absence of friction in the instrument is particularly advantageous.

The operations of lowering the annular foot onto the rubber and application of the 535-gram load are done in two steps, with a single lever. It is true that the intermediate position (which represents a reasonably large interval) when the annular foot is already resting on the rubber and the first reading is to be made, is not geometrically clearly defined, since it varies with the thickness of the test-specimen. However, with brief experience, the position of arrest of the micrometer in the optical field is observed immediately. The advantage of the simplicity and continuity of the operations is obviously convincing.

The instrument can be completely dismantled and remounted in a very short time; for example, for the purpose of checking by the binocular microscope whether the indentor is clean. The relocating in position of the micrometer is perhaps a little laborious, because it must be in perfect focus and because the scale must be exactly vertical. Practical tests made in different laboratories have had as their purpose the obtaining of evidence of any difficulties of reassembling after complete dismantling, provided that this happens to be necessary.

Light necessary for reading is obtained by an adjustable mirror, and any window or small lamp at a distance serves the purpose.

It has already been mentioned that the shear modulus derived by means of the formula of Scott from hardness measurements, with a time interval of 30 seconds between application of the total load and the second reading, is a static modulus. Yet in some of the most important applications of rubber, it is not the static modulus which is of importance, but rather the dynamic modulus.

There is, then, at least one limitation in making a hardness test; not in any way concerned with its previous application in rubber technology, but with respect to the more definite and important feature which has been discussed. Now, in comparative tests with a certain number of natural-rubber mixtures, the shear modulus derived from the depth of indentation in the hardness test and the modulus obtained by a hysteresometer with a frequency of 20 periods, are practically the same when the hardness of the vulcanizate is below 60 (see Figure 6).

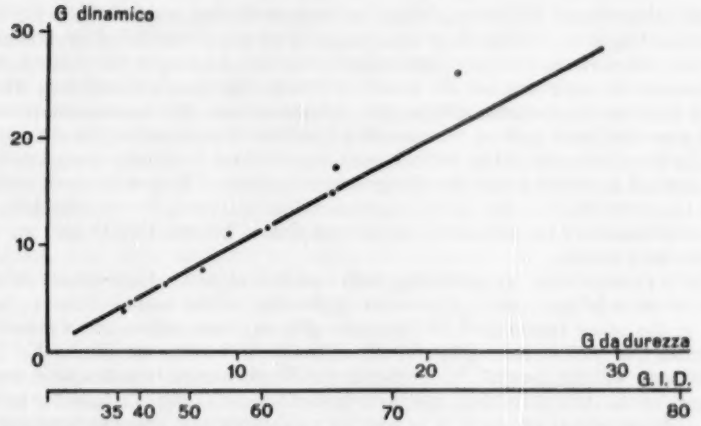


FIG. 6.—Comparison between the static modulus G derived from the measurement of hardness and the dynamic modulus G' (at 20 cycles per second), obtained with a hysteresometer, of some natural-rubber vulcanizates. The differences are important only for vulcanizates harder than 60. The lower abscissa scale is in IRHD.

There is, therefore, a wide range of vulcanizates for which the hardness test gives a satisfactorily approximate measure of the modulus, including the dynamic modulus, with exceptional rapidity and convenience of measurement. For other types of vulcanizates, there is a difference, and this may be considerable, but in this case the same phenomena of creep and after elastic effects are so complex that it is difficult to regard even a value for the dynamic modulus at a single fixed frequency as completely satisfactory.

There is, on the other hand, a problem which is a little perplexing and to which insufficient attention has so far been paid. Scott has shown the coincidence between the Shore A scale and the scale which we can hereafter call the international scale, using natural-rubber vulcanizates. In special tests in the

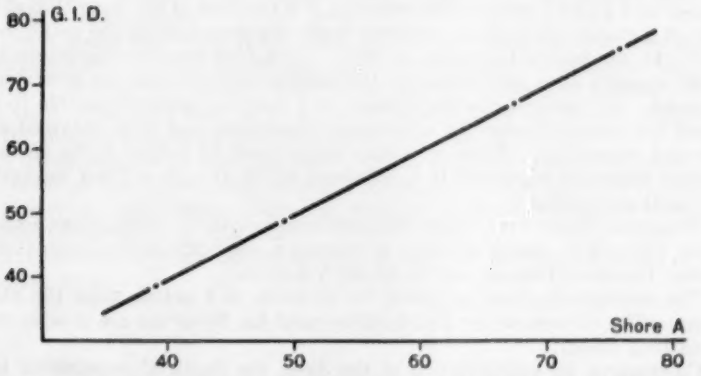


FIG. 7.—Comparison between values of Shore A hardness and International Rubber Hardness Degrees, obtained in comparative tests by several operators with four natural-rubber vulcanizates. Statistical analysis indicates the difference between the instruments at the level of 1 per cent as of no significance.

Pirelli laboratories, this coincidence has been confirmed several times for two significant figures. However, when synthetic rubber of the GR-S type is used for the comparison, this complete coincidence can no longer be verified, and differences of some degrees are found[5]. Often with synthetic rubbers which show marked visco-elastic effects, the differences are still more accentuated. It is true that each system of measuring hardness is independent in character, and in specifications and in testing, only one of them is usually designated as the method to be used, but the disagreement between different kinds of rubber and the restriction to the use of natural-rubber mixtures for the checking of Shore durometers by means of rubber samples of known IRHD lead to unsatisfactory results.

It is evident that, by operating with two techniques, which specify in one case 30 seconds' time interval between application of the load and the reading, and in the other case only 1 to 3 seconds (Shore A measurement as normally executed), a systematic accord for all materials will never be attained. The agreement will, in general, be better if the Shore measurement also is made longer (as the ASTM method specifies, up to 15 seconds, for example, by previous understanding) or else if it is possible to shorten also the measurement of hardness with the dead-load instrument.

TABLE 2

Vulcanizate	IRHD (30 seconds)	Shore value (1 second)	Difference
X-1	84	91	7
X-2	54	59	5
X-3	65.5	72	6.5
A (natural rubber)	59	58	−1
B (Butyl rubber)	56	58	2
C (natural rubber)	68	68	0
D (Butyl rubber)	66	68	2
E (Neoprene)	71	75	4
F (Vulcollan)	73	73	0

For a long time, a procedure of the second type has been in use in the Pirelli laboratories. Measurements of the depth of indentation read at 10, 30, and 60 seconds and 2 and 3 minutes are recorded as a function of the logarithm of the time on a graph. It is, then, relatively easy to extrapolate on the graph, both for short times and for long times, in order to bring out any possible intersection of the straight lines and change of the relative positions among several vulcanizates. In particular, extrapolation to 1 second makes it possible to approach the results obtained by a laboratory durometer and those obtained with a pocket durometer. What in certain cases must be judged to be an inadmissible difference is reduced to a difference which, though still not negligible, is at least acceptable.

We give in Table 2 the values obtained with a series of vulcanizates, some of which (X-1, X-2, and X-3) were of unknown composition, in International Rubber Hardness Degrees, and in Shore A degrees.

The hardness degrees are lower, by as much as 7 points, than the Shore values. The differences for Butyl rubber and for Neoprene are greater than for natural rubber.

Calculating, by extrapolation of the data, the depth of penetration to 1 second, the situation, though not completely standardized, is better, as shown in Table 3.

Only repeated tests would make it possible to establish the exact extent of the differences. However, in principle, the agreement between Shore measurements and International Rubber Hardness Degrees can be accepted as true of all vulcanizates if the associated after elastic effects are taken into account. The comparison can be applied also to plastic materials, e.g., plasticized polyvinyl chloride, but it is evident that, in the case of plastics, the tolerance in the lack of agreement, even by extrapolation, will be relatively great. The procedure can also be used to estimate values of the dynamic modulus, in a second approximation.

The two mathematical steps in passing from depth of indentation to modulus, and from modulus to degree of hardness, are quite independent. Having checked the validity of the formula of Scott, it is possible to obtain the same value of International Rubber Hardness Degrees by using a durometer with any ball diameter and any desired loads, within limits.

This might mean that it is possible to continue to use for this purpose numerous types of durometers which have appeared in various countries during the past twenty years. This is, however, really not to be recommended, because, in any event, secondary operating factors, such as the thickness of the

TABLE 3

Vulcanizate	IRHD (extrapolated to 1 second)	Shore hardness (1 second)	Difference
X-1	91	91	0
X-2	57	59	2
X-3	70	72	2
A	60	58	−2
B	58.5	58	−0.5
C	69	68	−1
D	69	68	−1
E	77	75	−2
F	74	73	−1

test-specimen and the use or non-use of an annular foot, would not be the same. To attain the maximum degree of reproducibility required by specifications, it is necessary that the instruments adopted conform to a mutual standard to the best possible degree.

There is one case where it has seemed useful to change the diameter of the ball and the load applied. In certain cases it is not possible to expect a thickness of 8 mm., or even of 4 mm. Vulcanizates may be in the form of films only 1 mm. thick, or of slabs from which films only 1 mm. thick can be cut, maintaining the thickness-width ratio of the reasonable value of 1:8 or 1:6.

A measurement of the hardness with an ordinary durometer when the sample is so thin is evidently out of the question. The use of a miniature durometer, having a ball of 0.5 mm. diameter and correspondingly reduced weights, is instead quite possible.

The formula of Scott can be written, in fact was originally written, in the following form:

$$P = 0.00051 \cdot G \cdot R^2 \left(\frac{H}{R}\right)^{1.35}$$

from which

$$G = \frac{1}{0.00051} \cdot \frac{P}{R^2} \left(\frac{R}{H}\right)^{1.35}$$

If R is reduced by $1:K$, and P instead by $1:K^2$, and the unit of measurement H also becomes $1:K$ with respect to the original value, the second member remains constant, and the same value is obtained for G. Passage from modulus to Hardness Degrees remaining unaltered, it is quite possible to construct a

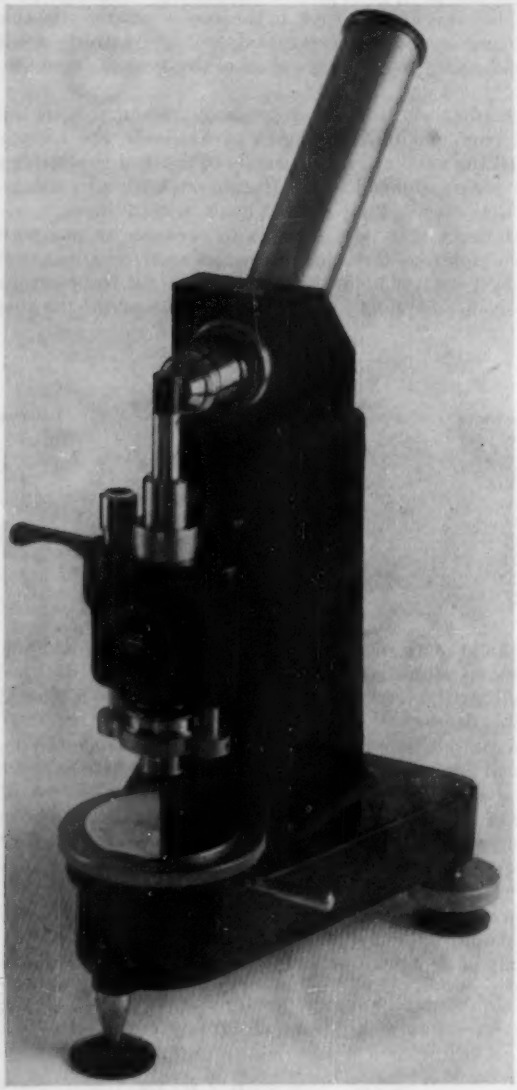


FIG. 8.—Microdurometer, studied in the Pirelli laboratories, for hardness tests of rubber whose thickness is of the order of 1 millimeter. The final expression of the results is still in International Rubber Hardness Degrees.

miniature durometer or microdurometer, with linear dimensions reduced by $1:K$ and with loads corresponding to the square of this ratio, and thus to obtain the same values in terms of Hardness Degrees of the material as when using the same tables for the conventional durometer. With a sphere of 0.40 mm. diameter, the total load used is 15.7 grams. The readings, taken in hundredths of a millimeter, are multiplied by 6 before using the data in Table 1, giving IRHD.

As a further comparison, the normal test-specimen for the miniature durometer should be 1.3 mm. thick.

An instrument of this type has been developed in the Pirelli laboratories. Figure 8 shows a general view of the instrument as constructed in its final form, while Figure 9 shows graphically the results of a series of measurements made in parallel on the same mixtures, vulcanized in different thicknesses, with the conventional durometer and with the microdurometer.

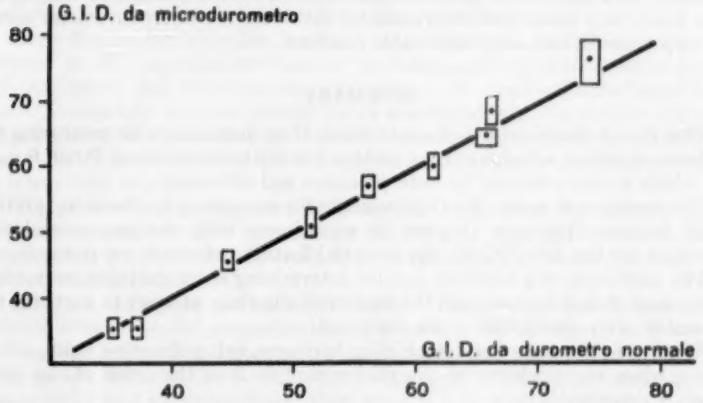


FIG. 9.—Comparison, made with a series of vulcanizates, between the values in IRHD obtained with a conventional durometer and test-specimen 8 mm. thick and with the microdurometer and test-specimen 1.3 mm. thick. The accord may be regarded as quite satisfactory.

The term microdurometer is perhaps an exaggerated expression, particularly if it is taken into consideration that microhardness measurements of steels and of alloys are made directly on single crystalline elements. Perhaps a similar microhardness measurement could be made on rubber if, as in the case of metallographic preparations, it were possible to make its surface perfectly smooth. But since this is not possible except by starting with the uncured compound, it was decided to go no further than an intermediate step which was feasible practically.

The manipulation of the ball of correct diameter, 0.40 mm., and fixing it with the necessary precision at the extremity of a straight and rigid stem of little greater diameter, without alteration of the front hemispherical surface, and reducing the end of the stem to 0.30 mm. so as to have no interference from it, constitute a test of patience and skill. Reading of the depths of indentation is more than ever to be made microscopically, but moderate magnification gives satisfactory sensitivity. This time a micrometer objective is not used, because, even if reduced to a glass disk of a few mm. diameter, its weight, which would be included in the "zero" load, would be excessive. Instead, an ocular micrometer is used, and on its scale, the movement of the upper end of the stem

of the indentor, in the form of a sharp point, is followed. The microscope, which in the conventional durometer is a part of the annular foot, in this case is separated from the foot because of its weight, and a second point attached to the annular foot to control its movement appears in the same field of vision.

As far as the microdurometer is concerned, if there can be any doubt about its future utility, this would be based not on the convenience of reading or on the practicability of the instrument, but on the fact that mere traces of rust, to be sought for with the binocular microscope, can change the front surface of the sphere and increase the friction of the stem. This would make necessary the adoption of special materials in pieces which are difficult to obtain even for less valuable materials.

By measuring hardness by the micromethod, it is possible to obtain data on the shear modulus of samples too small to be tested by any other mechanical method. In a laboratory where samples of complicated dimensions and, at the same time, very small size are frequently involved, the microdurometer serves not only a useful but an irreplaceable function.

SUMMARY

This report describes the characteristics of an instrument for measuring the hardness of rubber which has been designed in the laboratories of Pirelli S.p.A., and which is characterized by both precision and efficiency.

The instrument meets the requirements for measuring hardness in International Rubber Hardness Degrees in accordance with the recommendation developed by the ISO/TC 45, the essential features of which are summarized.

The usefulness of a hardness test for determining shear modulus, even when determined statically, and also the means of allowing, at least in part, for the associated after elastic effects are discussed.

Finally, a durometer for determining hardness, using the same units, and of service when the thickness of the rubber sample is of the order of one millimeter, is described.

REFERENCES

[1] Buist, "Hardness Testing of the Rubberlike State", Report of the General Conference of the British Rheologists' Club, London, Oct. 1946, p. 92.
[2] Table UNI 2034, issued in 1942.
[3] Scott, et al., *J. Rubber Research* **12**, 117 (1943); **13**, 19 (1944); **16**, 134 (1947); **17**, 1, 83, 145 (1948); **18**, 12 (1949).
[4] Schreuer, *Kolloid-Z.* **129**, 123 (1952).
[5] Soden, "Practical Manual of Rubber Hardness Testing", *India-Rubber J.* **119**, 27, 7 (1950); **120**, 9, 6 (1951).

RUBBER HARDNESS TESTING *

J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS,
SHAWBURY, SHREWSBURY, SHROPSHIRE, ENGLAND

Dictionaries give a confusing array of explanations of "hard" and "hardness". A hard material, according to the Oxford English Dictionary, is one "that does not yield to blows or pressure; not easily penetrated or separated into particles; firm and resisting to the touch . . .". "Hardness" implies "difficulty of penetration, inflexibility, rigidity, stiffness . . .".

Even the earlier scientific workers on rubber were equally vague; thus, Dawson[1] in 1927 regarded hardness as "an ill-defined little understood property" and considered that resistance to penetration—the practical criterion of hardness—"brings into play not merely forces associated with the surface cohesion, but also more deep-seated disturbances connected with elasticity, plastic deformation (or set), internal friction, resilience, and energy absorption"—truly an intractable mixture!

The practical man, disregarding theoretical difficulties, has always judged hardness by some form of indentation test, if only with the thumb-nail or a pencil point, and out of such crude beginnings have grown the precise standardized tests of today.

However, hardness testing could never have reached its present status without a fundamental understanding of the nature of the hardness of vulcanized rubber. The first important step towards this understanding was the study of the indentation of rubber by a rigid ball[2]. This demonstrated, both theoretically and experimentally, that when a ball of given diameter under a given force penetrates an elastic isotropic material, the depth of indentation is determined solely by the elastic modulus of the material.

A word of explanation may be added here about the term elastic modulus. The investigation just referred to was in terms of "Young's (extension) modulus for small strains", but since shear modulus is less dependent on the magnitude of the strain, it may be considered preferable to Young's modulus. Since, in an isotropic elastic material, shear modulus is one-third of Young's modulus, provided the strain is small, it is immaterial to the present argument which is used.

The important point is that hardness is a measure of elastic modulus, or more specifically, the load required to press a ball of given diameter to a given depth into a rubber is proportional to its elastic modulus. Two important consequences follow: First, it removes hardness testing from the realm of empiricism and gives it its rightful place among the quantitative measurements made on rubber; second, it has enabled a scientifically designed scale of hardness to be developed.

Actual rubbers are, of course, never perfectly elastic and isotropic. A well vulcanized "pure-gum" natural rubber comes very near to this ideal, but deviations from it increase as we pass to filler-loaded and synthetic rubbers and

* Reprinted from the *Rubber Age* of New York, Vol. 77, No. 4, pages 543–548, July 1955.

when we consider tests at low temperatures. However, provided these imperfections are not lost sight of, we shall not fall into serious error.

FACTORS INFLUENCING HARDNESS MEASUREMENTS

Before discussing the development of test methods and instruments, we must consider briefly certain factors that affect the result, since they have had an important influence on these developments.

Properties of rubber.—Among the properties of rubber, elastic modulus is of over-riding importance, as indicated above. However, all rubbers show some time dependence of deformation, resulting in creep and stress relaxation. Consequently, in an indentation test, the depth of indentation increases with the period of application of the load, so that for precise measurements the period must be fixed. Experiments have shown that 30 seconds suffices to reach a reasonably constant indentation in the usual form of indentation test[3].

The smoothness of the rubber surface has some influence; even a fine cloth marking appreciably increases the indentation[4]. Buffing with a fairly fine abrasive (60–80 mesh grit) avoids this, but the rubber must be given a rest period after buffing. Lubrication normally has little effect, but since it does tend to give more consistent readings[5], lubrication of the rubber surfaces with talc has been recommended as standard practice by the International Rubber Test Methods Committee ISO/T.C.45 (see Appendix, Section 3, Procedure).

Dimensions of the rubber.—Theoretically, the result of any indentation test depends on the thickness of the rubber, because indentation involves compressing it between the indentor and the underlying hard surface, and the thinner the rubber, the greater is the compressive strain produced by a given indentation. The effect of varying thickness can indeed be serious. The way towards minimizing this undersirable feature was shown by the discovery that the effect of varying thickness is less the smaller the diameter of the indentor (ball or cylindrical plunger)[6]. It is, of course, possible to correct approximately for variations in thickness. The British Standard hardness method includes a graph for this purpose[7], and similar data in tabular form have been published[8].

The lateral dimensions of the rubber have some effect in that a test near the edge gives a deeper indentation. This is more pronounced, the thicker the rubber; consequently the International method agreed by ISO/T.C.45 specifies a minimum distance from the edge for any given thickness (see Appendix, Table 1).

Temperature and humidity.—The effects of these external variables have not been fully studied, but in so far as they affect modulus or creep, they must influence the hardness reading. Consequently, control of temperature within certain limits is essential. (ISO/T.C.45 recommends a tolerance of $\pm 2°$ C; see Appendix, Section 6). Whether humidity need be controlled is still an open question. In a different sense, the effect of temperature is useful because it forms the basis for using hardness tests to study cold resistance of vulcanized rubbers.

HARDNESS TESTS AND INSTRUMENTS: GENERAL CONSIDERATIONS

There is no need here to describe the many instruments devised for testing hardness of vulcanized rubber, since an excellent survey has recently been published[9]. It will suffice to state that, with very few exceptions, all hardness instruments have used the principle of pressing a rigid indentor into the rubber.

One interesting exception is the Herbert pendulum, in which the hardness of the rubber is made to influence the time of swing of a rocking pendulum[10]; however, this has never been widely used in rubber testing. We must now consider in detail the essential factors in penetration tests.

Shape of indentor.—Indentors so far used have been spherical (or part-spherical in the form of hemispherical-ended plungers), conical, frusto-conical (as in the Shore durometer), or flat-ended cylindrical plungers.

Two considerations, one theoretical and one practical, influence the choice of indentor shape. The theoretical consideration is the relation between the

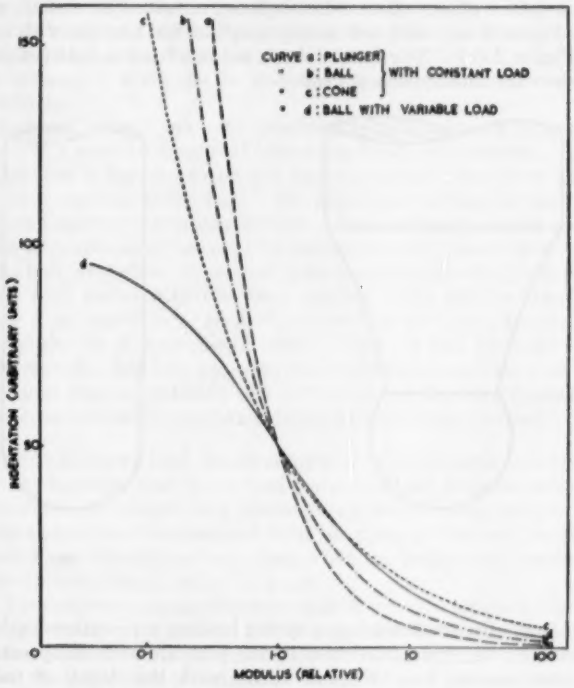


FIG. 1.

modulus of the rubber and the depth of indentation under a fixed load. It would be very convenient to have a hardness scale such that equal proportionate differences in modulus produce equal differences in hardness reading. Since the quantity read directly is usually the indentation, the ideal would thus be a linear relation between the logarithm of the modulus and the indentation. The actual relationships for the three mean types of indentor are shown in curves a, b and c of Figure 1 (the frusto-conical indentor probably behaves similarly to the flat-ended cylindrical plunger).

None of the indentors comes near to the ideal linear relation, but the cone is the nearest, while the flat-ended plunger is worst, giving a very cramped scale in the high modulus region and an unduly open scale in the soft region. How-

ever, practical considerations argue strongly against any indentor with a sharp point (cone) or edge (plunger), because wear or damage of the point or edge is inevitable and influences the behavior of the indentor. It is well known that such wear occurs in the Shore durometer, and leads to incorrect readings. Ball or hemispherical-ended indentors are much less subject to this disadvantage. This, and the fact that hard steel balls of very accurate diameter as made for use in bearings are readily available, indicates the ball as the most suitable type of indentor, thus endorsing the choice already made by most national standardizing organizations.

An important detail in the design of a ball indentor is that it should comprise a part-sphere greater than a hemisphere, mounted on a shaft of reduced diameter—Figure 2 (a)—and not merely a cylindrical plunger with hemispherical end—Figure 2 (b). The former shape reduces friction between rubber and indentor when the indentation is deep.

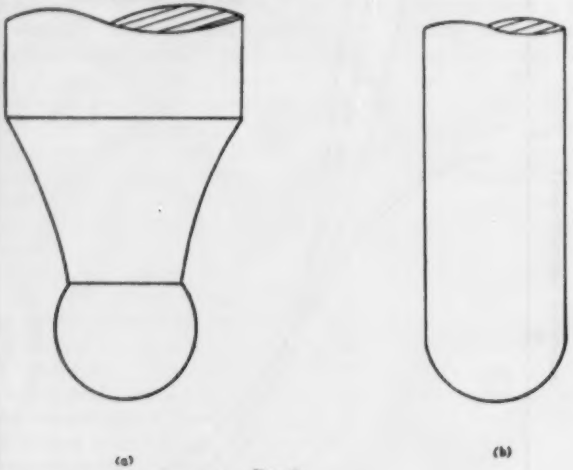


FIG. 2.

Type of load.—Instruments using spring loading are—either deliberately or owing to the unavoidable variation of spring pressure with compression—variable-load instruments, i.e., the load varies with the depth of indentation. Dead-load instruments give nominally a constant load, although, in fact, variation is often introduced by the spring in the dial measuring gauge.

A variable load has one theoretical advantage in enabling a nearer approach to the ideal linear relation between log. modulus and indentation, as referred to above. Curve d in Figure 1 shows this relation for a ball indentor with a load that varies linearly from a maximum at zero indentation to zero at a limiting maximum indentation. Although still not straight, this line comes nearer to having a uniform slope than do any of the curves (a, b, c) for indentors used with a constant load.

However, the variable-load principle has practical disadvantages, especially if one adopts the obvious simple method of producing a load that varies automatically and linearly with the depth of indentation, i.e., by using a spring. To get a spring giving exactly the right load/indentation relationship, and to

readjust it if fatigue or other cause upsets it, is far less easy than providing a dead weight for a constant-load instrument. Consequently, all precision laboratory hardness gauges have adopted the dead-load principle.

It is appropriate to mention here one important type of variable-load instrument, namely, that developed by Buist and Kennedy[11], in which the load is deliberately variable so as to produce a constant indentation, the hardness being thus measured in terms of a force, not an indentation. The advantage is that the force so measured is (for an elastic isotropic material) strictly proportional to the elastic modulus, provided all rubbers tested have the same thickness, whereas the generally accepted indentation/modulus relationship is only approximate unless the rubbers tested are extremely thick. Hence, when it is desired to use hardness tests to measure modulus, this constant indentation test is preferable. It has not, however, been widely adopted for general purposes, doubtless because it is simpler to measure an indentation than to adjust and measure a force.

Zero load and presser foot.—All hardness tests involve an indentation, and the depth of this must be measured from some fixed zero position. This sounds quite simple, but in fact the fixing of a satisfactory zero has given more trouble than any other feature of the test. The ideal zero position would be with the indentor just touching the rubber surface. Unfortunately, with a ball indentor this proves impracticable, because, to ensure contact, some force must be applied to the ball, and since the contact area is extremely small, this produces an indentation that varies with the force applied. (As will be noted later, the indentation P is proportional to $F^{0.74}$, where F is the force; hence, dP/dF approaches infinity as F approaches zero.) Thus, it will be difficult to get a sufficiently reproducible zero position, and experience confirms that taking the position of first contact between ball and rubber as the zero is unsatisfactory.

Two alternative solutions of this difficulty have been devised:

Zero Load: A known load (small compared with the main indenting load) is applied to the indentor and its position under this load is taken as the zero.

Presser Foot: An annular foot, surrounding the indentor, rests on the rubber surface; the indentation is measured from the plane of this foot, on the assumption (which is not necessarily true) that, when the indentor is just touching the rubber, its tip is in this plane.

It has been shown in a recent paper[5] that in practice either of these methods is liable to give inaccurate results, for reasons fully discussed therein and hence not reproduced here. This paper further shows theoretically, and confirms by experiment, that the best procedure is to use both a presser foot and a zero load; that is, indentations are measured from the flat surface of a rigid foot resting on the rubber, and the reading taken is the difference between identations produced by a small zero load and a large total load. This is the preferred method in the British Standard (B.S. 903: 1950) and has since been adopted by the International Committee ISO/T.C.-45 (see Appendix, Section 3).

The British Standard, but not the ISO method, does make possible tests without a foot, referred to as base-plate tests, because indentations are measured relative to either the base plate that carries the test-piece (e.g., Admiralty gauge) or the supporting surface—not part of the instrument—on which both instrument and test-piece rest (e.g., Pusey-Jones). However, this form of test is restricted to rubber articles of which the upper surface is not flat, so that a foot would not rest firmly on it.

Expression of hardness.—From almost the earliest days of hardness testing, some instruments have expressed hardness directly as depth of indentation, so that zero hardness is in fact infinitely hard, while others have reversed the scale, taking an arbitrary 100 as dead hard, with 0 for very soft. This has led to much confusion, and after a prolonged attempt in the United Kingdom to get the former type of scale generally adopted (the British Standard Hardness Number of B.S. 903: 1940), it had to be realized that the practical man, especially the engineer, did not readily accept zero hardness as signifying infinitely hard. In the 1950 British Standard, therefore, the scale was reversed and this scale, ranging from 0 (infinitely soft) to 100 (infinitely hard), is now accepted internationally, as will be described below.

THE BALL INDENTATION TEST

We thus reach the conclusion that the best test for general purposes is with a ball indentor, surrounded by a presser foot that forms the reference plane for indentation measurements, and in which the difference between the indentations under a small zero load and a large total load is measured and then transformed into a value ranging between 0 (soft) and 100 (hard). It now remains to consider the details, such as size of ball, foot size and pressure, indenting loads, and method of transforming readings.

Ball size.—The first factor to be considered is the desirability of making the test as nearly as possible insensitive to variations in the thickness of rubber tested. It has been shown[6] that to do this the indentor should be as small as possible. However, too small a ball is undesirable for the following reason: The indentation (P) produced by a ball of radius R is related to the indenting force (F) and the Young's modulus of the rubber (M) as follows[2]:

$$F/M = K \cdot R^{0.65} P^{1.35} \qquad (1)$$

where K is about 1.9 (a revision of the originally published value 2.1) when all quantities are in c.g.s. units[12].

Equation (1) is true only when P is less than about 1.6 R, so that the ball diameter should be at least 1½ times the deepest indentation normally encountered[13]. At the time this matter was being considered by the British Standards Institution, hardness was expressed as a depth of indentation, and it was desired that this should be the same as with a ¼-inch ball under 1 kg. load. This means having indentations up to about 1.9 mm., and hence a ball not less than about 2.4 mm. diameter.

As the ASTM had already standardized 3/32-inch (2.38 mm.), this size was adopted by the British Standards Institution. In subsequent international discussions this was changed to 2.44 ± 0.06 mm., to allow the standard metric 2.50 mm. ball to be used. The variation in hardness readings produced by the tolerance is of no account in view of other unavoidable sources of variation.

Indenting loads.—The larger the load, the deeper the indentation and, hence, the more accurately it can be measured. However, if the indentation is deep it becomes more sensitive to variations of thickness of the rubber[6]. This was another reason why the British Standards Institution, in adopting the ASTM 3/32-inch ball, did not adopt the 3 lb. (1360 g.) load, which would have given a much deeper indentation than the test with a ¼-inch ball and 1000 g. load. The decision to keep the same indentation as in this latter test necessitated reducing the load far below 1000 g.

The next point was to decide on the zero load. This was again a com-

promise. If the zero load is too large, the total indentation is increased, and the test is thus made more sensitive to thickness variations. If it is too small, the zero indentation becomes very sensitive to any error or variation in the zero load (since dP/dF is high when F is small). The best compromise was decided to be about one-twentieth of the total load[14].

These considerations led to the choice of 30 g. zero load and 570 g. total load for the I.S.O. ball of 2.44 mm. diameter.

Foot dimensions and pressure.—The deformations produced by pressing a ball into a piece of rubber are not confined to the immediate vicinity of the ball. The rubber that has been forced out of the space occupied by the indentation must go somewhere, and it is likely that this results in a slight thickening of the rubber at some distance from the indentor. If a foot is pressing on the rubber this thickening will be resisted, and this will react on the indentor in the sense of reducing the depth of indentation. This theoretical deduction is confirmed by experiments[15] which show that, with a 3/32-inch ball, the differential indentation reading (using 30 g. and 565 g. loads) is reduced about 7 per cent by the use of a foot 0.8 inch diameter with central 0.2 inch hole under a pressure of 850 g. It is thus important to standardize the dimensions and pressure, and this has been done by the International Committee ISO/T.C.45 (see Appendix, Section 2d).

Vibration and lubrication.—Most hardness instruments use a dial micrometer gauge to measure the indentation. This and other moving parts introduce the possibility of friction and, hence, inaccurate readings. Gentle vibration, e.g., by an electric buzzer, helps to overcome this and has been shown to improve the consistency of readings very considerably[5]. Lubrication of the rubber surfaces with talc gives a further small but definite improvement. The ISO Committee therefore recommends such lubrication, as well as the application of gentle vibration in all instruments where there is any possibility of friction.

Choice of hardness scale.—In devising a hardness scale, several features were held to be desirable:

(1) The scale should extend from 0 (infinitely soft) to 100 (infinitely hard).

(2) The hardness value should bear a known relation to modulus in the case of elastic isotropic materials.

(3) Over at least the central range of values, one unit difference in hardness should correspond to the same proportionate difference of modulus (i.e., hardness should be a linear function of log. modulus).

(4) The scale should if possible approximate to the Shore A scale.

Fortunately, it proved possible with a little ingenuity to satisfy all these requirements reasonably well. This was achieved by using a probit (integrated Gaussian error) curve to transform log. modulus into a hardness value. The curve actually used is shown in Figure 1 of the Appendix. This has its midpoint (hardness 50 degrees) at log. $M = 2.50$ ($M = 315$ lb./in.^{2}) and a maximum slope (at the midpoint) of 54 degrees per 1 unit difference in log. M. For those who like precise definitions, the International Rubber Hardness Degrees (IRHD) value is the percentage frequency corresponding to a probit value equal to $(1.352 \log_{10} M + 1.620)$, where M is the Young's modulus in lb./sq. in. of the rubber. (If shear or rigidity modulus G is used instead of M, the formula becomes $1.352 \log_{10} G + 2.097$). Probit is defined thus[16]: The probit of the proportion P is the abscissa which corresponds to a probability P in a normal distribution with mean 5 and variance 1.

THE I.S.O. RECOMMENDED TEST

Frequent reference has been made above to the hardness test method agreed by Committee ISO/T.C.-45, Rubber, of the International Organization for Standardization (I.S.O.), which is reproduced in full in the Appendix. This incorporates the recommended test conditions described above. It was accepted as a Final Draft ISO Proposal at the 1951 (Oxford, England) meeting and slightly revised at the 1953 (Paris, France) meeting. It is important that this method should be made known and used as widely as possible, so as to encourage uniformity of practice among all those concerned with hardness testing of rubber.

It has been indicated above that the International Rubber Hardness Degrees (IRHD) scale used in the ISO method was designed to agree approximately with the readings of a Shore A Durometer made strictly in accordance with the ASTM standard[17], i.e., having a maximum indentor protrusion of exactly 0.100 inch. Exact agreement is not possible over the whole range of hardness because by definition zero IRHD represents a material of zero elastic modulus, while zero Shore corresponds to a finite modulus, so that on very soft rubbers the two scales cannot agree.

Exactly how near the agreement is in the more normal hardness range depends on what is taken as the true Shore reading. The tolerances on indentor diameter and protrusion and spring calibration allowed by ASTM D676-49T together result in a variation of up to 5 degrees in the reading, and different laboratories using the same Shore instrument have been found to differ (on soft rubbers) by 2 or 3 degrees, even though each has averaged the results for several operators agreeing well among themselves. Moreover, the relation between Shore and IRHD is not the same for different polymers; thus, GR-S will generally read about 2 degrees higher on the Shore instrument than a natural rubber of the same IRHD value.

The position can best be summarized by saying that, except for very soft rubbers, the IRHD reading will generally lie within the range of Shore readings resulting from the sources of variation indicated above, but towards the upper end of this range. For very soft rubbers, the IRHD reading must be higher than Shore for the reason explained above.

APPENDIX

FINAL DRAFT I.S.O. PROPOSAL FOR THE DETERMINATION OF HARDNESS

The standard hardness test is based on a measurement of the penetration of a rigid ball into the rubber test-piece under specified conditions. The measured penetration is converted into International Rubber Hardness Degrees, the scale of degrees being so chosen that 0 represents a material having an elastic modulus of zero and 100 represents a material of infinite elastic modulus, and so that the following conditions are fulfilled over most of the normal range of hardnesses:

a. One International Rubber Hardness Degree always represents approximately the same proportionate difference in Young's modulus.

b. Readings in International Rubber Hardness Degrees are approximately the same as those of the Shore Durometer Type A.

For substantially elastic isotropic materials, like well-vulcanized natural rubbers, the hardness in International Rubber Hardness Degrees bears a known relation to Young's modulus, although for markedly plastic or anisotropic rubbers the relationship will be less precisely known.

TABLE I

Total thickness of test-piece		Minimum distance	
(mm.)	(in.)	(mm.)	(in.)
2.5	0.1	6.5	0.25
5	0.2	7.6	0.30
8	0.3	9.0	0.35
10	0.4	10.0	0.40
15	0.6	11.5	0.45
25	1.0	12.7	0.50

The hardness test consists of measuring the difference between the depths of penetration of the ball into the rubber under a small initial load and a large final load. From this difference, the hardness in International Rubber Hardness Degrees is derived by using either Table II, or a graph based on this table, or a scale, reading directly in International Rubber Hardness Degrees and derived from the table, fitted to the penetration-measuring instrument.

TABLE II

D(mm/100)	International rubber hardness degrees	(Dmm/100)	International rubber hardness degrees
0	100.0	80	57.0
10	96.6	90	53.3
20	89.9	100	50.0
30	83.0	120	44.2
40	76.6	140	39.5
50	70.9	160	35.5
60	65.7	180	32.5
70	61.1	200	30.5

The relation between the difference of penetration and the hardness expressed in International Rubber Hardness Degrees is based on:

(1) The known relation between penetration (P, in hundredths of a millimeter) and Young's modulus (M, in kilograms per square centimeter) for a perfectly elastic isotropic material, namely:

$$F/M = 0.00017\ R^{0.65}\ P^{1.35}$$

where F = indenting force (kg), and
R = radius of ball (cm.).

Note: This formula is approximate and is included as an indication.

(2) Use of a probit (integrated normal error) curve to relate $\log_{10}M$ and the hardness in International Rubber Hardness Degrees, as shown in Figure 1, this curve being defined thus:

a. Value of $\log_{10}M$ corresponding to midpoint of curve = 2.50 (i.e., M = 315 lb./sq. in.).

b. Maximum slope = 54 International Rubber Hardness Degrees per unit increase in $\log_{10}M$.

Test-piece.—The test piece has its upper and lower surfaces flat, smooth, and parallel to each other; two pieces of rubber (but not more than two) may be superimposed to obtain the necessary thickness.

The standard test-piece is between 8 and 10 mm. thick, the lateral dimensions being such that no test is made at a distance from the edge less than that shown in Table I.

Non-standard test-pieces may be thicker or thinner than the standard, but in no case less than 2 mm. thick. The lateral dimensions are such that no test is made at a distance from the edge less than that shown in Table I.

Tests intended to be comparable must be made on test pieces of the same thickness.

Apparatus.—The essential parts of the apparatus are: (a) A vertical plunger terminating in a rigid ball 2.44 ± 0.06 mm. diameter.

(b) Means for applying loads of 30 g. and 570 (± 5) g. to the ball; it is essential to allow for the weight of the plunger and any fittings attached to it and for the force of any spring acting on it, in order that the loads actually applied to the ball shall be as specified.

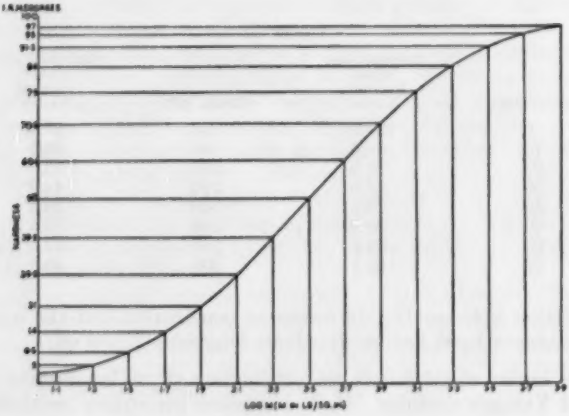


FIG. 1.

(c) Means, e.g., a dial gauge, for indicating the movement of the plunger, either in metric or inch units or reading directly in International Rubber Hardness Degrees.

(d) A foot about 20 mm. diameter normal to the axis of the plunger, and having a central hole about 5 mm. diameter for the passage of the plunger, the foot forming part of the position-measuring gauge; the foot rests on the test-piece and exerts a pressure on it of 200 to 300 g./sq. cm.

(e) Means, e.g., an electrically-operated buzzer, of gently vibrating the apparatus to overcome any slight friction (this can be omitted in instruments where friction is completely eliminated).

Procedure.—The test-piece is first conditioned. (See note.) The upper and lower surfaces of the test-piece are lightly dusted with talc and the test-piece supported on a horizontal rigid surface. The foot is first lowered to rest on the surface of the test-piece. The plunger and indenting ball are pressed for five seconds vertically on to the rubber, the load on the ball being 30 g.

If the gauge is graduated directly in International Rubber Hardness Degrees the bezel of the gauge is then turned so that the pointer indicates 100 (care being taken not to exert any vertical pressure on the gauge). An additional load of 540 (± 5) g. is then applied and maintained for 30 seconds; the reading on the gauge is the hardness in International Rubber Hardness Degrees.

During the loading periods, the apparatus is gently vibrated to overcome any friction.

If the gauge is graduated in metric or inch units, the movement of the plunger (D) caused by applying the 540 g. load as described above is read off and converted into International Rubber Hardness Degrees by using Table II or a graph constructed therefrom.

Number of readings.—One measurement is made at each of four or more different points distributed over the test-piece and the results are averaged.

Conditioning.—The samples are maintained at the temperature of test, and at a relative humidity still be be agreed, for at least 12 hours immediately before testing.

Temperature of test.—Normally the test is carried out at 20°(± 2)° C (see note).

Expression of results.—Hardness is reported to the nearest whole number as the mean result of the four (or more) measurements expressed in International Rubber Hardness (I.R.H.) Degrees, and the following additional data quoted:

(1) Thickness of test-piece.
(2) Temperature, if other than 20°(±2°) C.

(NOTE: Details of conditioning have not yet been finalized; in particular, the standardization of test temperatures is receiving further consideration[18].)

REFERENCES

[1] Dawson, *Trans. Inst. Rubber Ind.* **3**, 217 (1927).
[2] Scott, *Trans. Inst. Rubber Ind.* 11, 224 (1935).
[3] Dock, *J. Rubber Research* 13, 19 (1944).
[4] Dock and Scott, *J. Rubber Research* 16, 134 (1947).
[5] Scott, *Trans. Inst. Rubber Ind.* 28, 249 (1952).
[6] Scott, *J. Rubber Research* 17, 1, 9 (1948).
[7] British Standard Methods of Testing Vulcanised Rubber, B.S. 903-1950.
[8] Anon., *India-Rubber J.* 105, 59 (1943).
[9] Soden, "A Practical Manual of Rubber Hardness Testing", Maclaren & Sons, Ltd., London, England, 1951.
[10] Hills and Scott, *J. Rubber Research* 16, 141 (1947).
[11] Buist and Kennedy, "Facilities Available for the Physical Testing of Rubber in the Rubber Laboratories at Blackley", Bulletin, Imperial Chemical Industries, Ltd., Manchester, England. See also Soden, "A Practical Manual of Rubber Hardness Testing", Maclaren & Sons, Ltd., London, England, 1951, p. 26.
[12] Larrick, *Phys. Rev.* 57, 358 (1940).
[13] Scott, *J. Rubber Research* 17, 83 (1948).
[14] Scott, *J. Rubber Research* 17, 87 (1948).
[15] Soden, *J. Rubber Research* 20, 46 (1951).
[16] Finney, "Probit Analysis", Cambridge University Press, Cambridge, England, 2nd Ed., 1952.
[17] American Society for Testing Materials, ASTM Designation D676-49T.
[18] Buist, *India-Rubber J.* 125, 418 (1953).

ABRASION AND SLIPPAGE *

G. Ebert and V. Weidner

Experimental Rubber Laboratory, IG.-Farbenindustrie A.-G., Werk Badische Anilin- und Soda-Fabrik, Ludwigshafen A. Rh., Germany

INTRODUCTION

The types of apparatus used technically for testing the abrasion resistance of rubber compounds, in particular tread compounds, have been equipped to operate with 100 per cent slippage. The results obtained under such conditions seldom agree with the results of road tests, because the abrasion of tires under ordinary conditions takes place with relatively little slippage. No method for determining abrasion which takes this fact into account has yet come to the attention of the authors. Although the present work is already rather old, its publication still seems justified, since it focusses attention on some still unpublished results which are essential to any estimation of the practical behavior of tread compounds when subjected to abrasion.

EXPERIMENTAL TECHNIQUE AND TESTING EQUIPMENT

The testing machine described in the present paper was developed to determine the abrasion of tread compounds of rubberlike character. A ring test-specimen (the inner Schopper ring was used) runs at higher speed under friction on the front of an abrasive or emery wheel rotating about a horizontal axis. The degree of slippage can be changed by varying the speed of rotation of the grinding wheel. The following equation serves to visualize the friction quantitatively:

$$S = \frac{v_1 - v_2}{v_1} = \frac{n_1 R_1 - n_2 R_2}{n_1 R_1}$$

Here v_1 is the peripheral speed of rotation of the rubber ring.

v_2 is the peripheral speed of rotation of the abrasive wheel.
n_1, n_2 are the number of revolutions in a unit of time.
R_1, R_2 are the corresponding radii.

The quantity S is called the slippage. In absolute terms, it is $0 \leqq S \leqq 1$ or, in percentage: $0 \leqq S\% \leqq 100$.

In most machines, S is 1, or 100 per cent i.e., these machines operate with 100 per cent slippage. The slippage values of the machine to be described lie between zero and 24 per cent. The speed of the machine can also be varied in the ratio 2:3:4, independently of the slippage.

The advantage of the new method of measuring abrasion is that the mechanical stressing of the rubber can be changed through a wide range by varying the speed and slippage.

* Translated for Rubber Chemistry and Technology from *Kautschuk und Gummi*, Vol. 7, No. 9, pages WT 191–196, September 1954. The work was carried out in 1936–1937, but for the reasons given in the Introduction, the investigation remains an important contribution.

DESCRIPTION OF THE MACHINE

The whole mechanism is mounted on a frame G of vertical iron plates 6 mm. thick and 55 mm. apart. The drive shaft AA supports the driving gear AR, a sprocket wheel KR and two more gears, Z_1 and Z_2. The gear Z_2 transmits the motion through a gear Z_3 to abrasive wheel SR. The latter two gears are interchangeable. Gear Z_1 works through gear Z_4 to a countershaft HA with a gear Z_5. This latter transmits the motion through a gear Z_6 to the sprocket wheel KR and then to the test-wheel PR. The countershaft HA has a larger angular velocity (K = 31:12 = 2.583) than the drive shaft. The test wheel PR is mounted in a frame B, which is rotationally movable on the drive shaft AA so

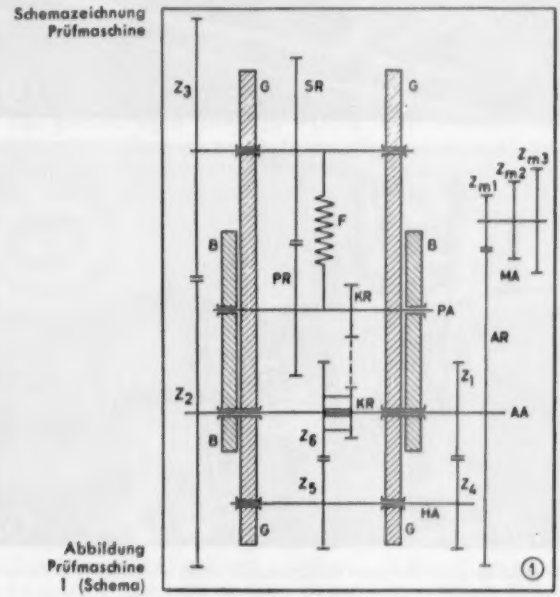
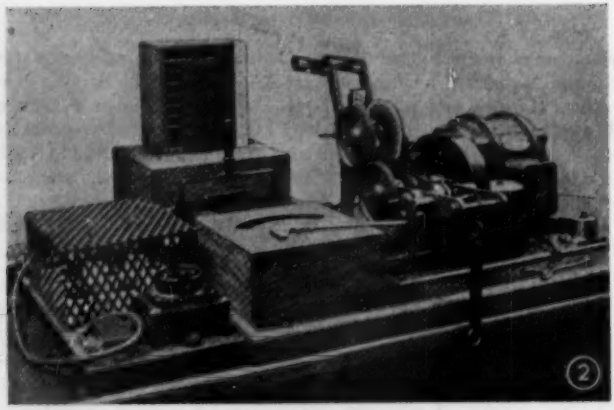


FIG. 1.—Schematic representation of the rubber testing machine.

that the test wheel is pressed against the abrasive wheel by a spring F. The specific surface pressure can therefore be varied within wide limits by extending the spring.

By means of the countershaft HA, transmission of movement to the test wheel without any twisting moment is assured. Proof of this is the fact that the abrasion is the same for both forward and backward running of the machine.

With the diameter of the abrasive wheel constant, the slippage can be varied by varying the angular speed of the abrasive wheel, which is done by pairwise changing of gears. The necessary variation of the axial distance is taken care of at the axle of the abrasive wheel. In this way it is possible to cover the entire range of slippage with a single abrasive wheel. The numbers of teeth of the interchangeable gears Z_2 and Z_3 are: 100, 102, 104, 106, 107, 108, 112, and 118. The corresponding values for the slippage are shown in Table 1.



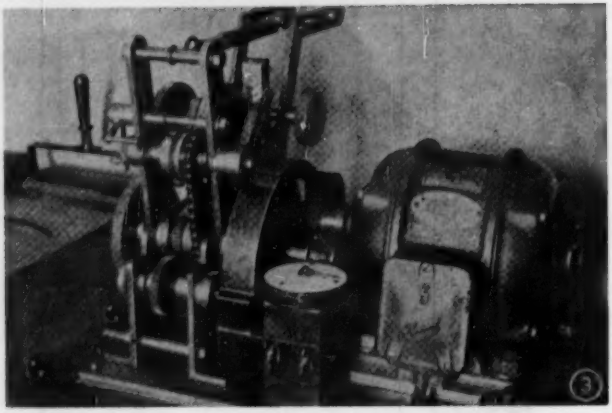


FIG. 2.—Photograph of the rubber testing machine shown schematically in Figure 1.

FIG. 3.—Photograph from a different view from that in Figure 2 of the rubber testing machine shown schematically in Figure 1.

TABLE 1

NUMBER OF TEETH OF GEARS Z_2 AND Z_3 AND THE CORRESPONDING SLIPPAGE VALUES

$\frac{Z_2}{Z_3}$	S (in %)	$\frac{Z_2}{Z_3}$	S (in %)
100/118	24.0	102/100	8.7
100/112	20.0	104/100	6.9
100/107	16.3	106/100	5.1
100/104	13.8	107/100	4.2
100/102	12.3	108/100	3.3
100/100	10.4	112/100	0

Diameter of abrasive wheel 113.5 mm. K = 2.583.
Diameter of rubber ring 49.0 mm. Redurit abrasive wheel.

The machine is driven by an alternating-current motor, MA, 200 watts, 910 r.p.m., which is mounted on a common base plate, 35 × 45 cm., on a slide so that it can be moved unidirectionally in order to change the velocity. Three gears are mounted on its shaft, Z_{m1}, Z_{m2}, and Z_{m3} the numbers of whose teeth are in the ratio 2:3:4. The speed of the machine can be increased proportionately. The number of revolutions of the machine is measured by a revolution counter coupled to the drive shaft; the time of an experiment is determined by a stopwatch. A watt-meter connected into the electric circuit measures the power while the machine runs with and without load, and also measures the work of friction as related to slippage, velocity, and specific surface pressure.

THE TEST-SPECIMEN

The specimen to be tested for abrasion—an inner Schopper ring—is a rubber ring of 37 mm. inside diameter, 44–45 mm. outside diameter, and with a width of about 4 mm. For testing, the ring is drawn over a spindle of 42 mm. diameter and pressed tight sideways with a nut. A brass washer inserted between the nut and the ring prevents the specimen from turning out of the channel thus formed when the nut is tightened. Since the ring is stretched about 10 to 15 per cent, it can not jump out, even at high speeds. The diameter of the extended ring is 49.5–49.8 mm. and the height of the projecting part about 2.0–2.5 mm.

According to the equation:

$$S = \frac{v_1 - v_2}{v_1} = \frac{n_1 R_1 - n_2 R_2}{n_1 R_1}$$

the diameter of the rubber ring governs the slippage; strictly speaking, the diameter of the ring ought not to change during the experiment, since every change of diameter results in a change of slippage.

In practice, the technique is as follows: The stretched ring is abraded with 24 per cent slippage for a definite period of time in order to reduce its diameter to about 49.3 to 49.4 mm.; the surface of the ring is roughened automatically in this process and thus prepared for the measurement itself. Measurement of abrasion is begun at the highest slippage, $S = 24$ per cent. The experimental time is optional, usually about half a minute. It should be short in order to keep the diameter of the ring as little changed as possible, but experimental accuracy should not be sacrificed. The successive slippage values are 20, 16.3, 13.8, 12.3, 10.4, 8.7, 6.9, 5.1, 4.2, and 3.3 per cent, while the times of measurement can be gradually increased to 2 minutes as the value of slippage decreases. If the abrasion is determined for all slippage values, the diameter of the ring is about 49.0–49.1 mm., in order that the actual slippage values agree exactly with the calculated values. The deviation of the actual slippage from the calculated value in the first measurements (diameter = 49.3 mm.) is about 0.5–0.6 per cent, and can be disregarded at S values of 20 to 24 per cent.

DESCRIPTION OF THE EXPERIMENTAL PROCEDURE

After the test-ring is reduced to the indicated diameter of 49.3 mm. by preliminary abrasion, the actual abrasion measurements are made with the different values of S. The dynamometer is adjusted to the exact tension and the motor is switched on, using a stopwatch. During the experimental run, the abrasive wheel and the rubber ring are both cleaned of coarse particles, which

might protect the ring from further abrasion, by small brushes lightly treated with chalk. At the same time the power requirement L_a of the motor is read on a wattmeter and recorded. After the measurements are made, the power L_0 for the unloaded system is determined, after removal of the friction, which can be done quickly by shifting a gear on the auxiliary axle without changing gears. The difference between the readings:

$$L_a - L_0 = L$$

is, within reasonable approximation, the work of abrasion in arbitrary units. The ring is spread with soft chalk all over and any abraded rubber is removed with the thumb and forefinger or mechanically. The ring is weighed, before and after testing, on an analytical balance. It is cleaned until the weight is

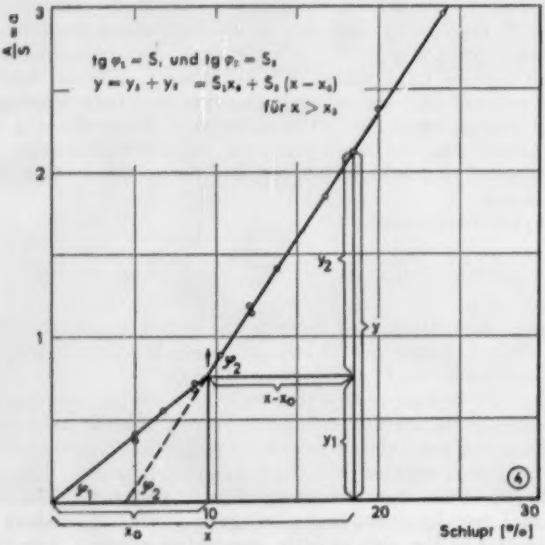


FIG. 4.—Abrasion-slippage characteristics. (P = 2; r.p.m. = 182; Redurit abrasive wheel.) The abscissa represents the slippage in percentage.

constant. This usually requires two applications. The weight loss obtained is finally converted to the basis of unit of time (one minute). The reproducibility of this abrasion measurement is very good. The accuracy can be increased considerably by repeated measurements or by operating with small slippage increments. Dulling of the abrasive wheel, i.e., decrease of abrasion, has not been observed, even in the course of months. It is recommended not to extend an individual measurement over a long period, since otherwise at small slippages proportionality between abrasion and time is no longer certain because of the formation of a protective layer against abrasion.

EXPERIMENTAL RESULTS

Instead of plotting the abrasion value A converted to a basis of unit time, it seemed more useful to plot the value of $\alpha = A/S$ against the slippage as in-

dependent variables. The value of α will be called the reduced abrasion. Table 2 gives a representative series of measurements, and Figure 4 shows the same data graphically.

The reduced abrasion values lie on a straight line which passes through the origin and deflects upward at a slippage value of x_0. The conformity of the experimental points with a smooth curve is good throughout the range of slippage. The abrasion-slippage graph can be regarded as characteristic of a product. Its analytical representation for $x > x_0$ is: $y = S_1 \cdot x_0 + S_2(x - x_0)$, where x is the variable slippage, y is the variable reduced abrasion, x_0 the abscissa value of the break in the curve, and S_1 and S_2 the slope factors of the lower and upper branches of the curve (see also Figure 4). The factors S_1, S_2, and x_0 are obviously material constants, something like the index of refraction in optics or loss angle or dielectric constant in electricity.

We shall call S_1 the lower abrasion coefficient and S_2 the higher abrasion coefficient of the material; the value x_0 is the transition point. The abrasion

TABLE 2

REPRESENTATIVE SERIES OF MEASUREMENTS

Time in minutes	Z_2 / Z_1	S(%)	A_{ms} (min.)	$\frac{A}{S}$
1/2	100/118	24.0	70.5	2.94
1/2	100/112	20.0	47.0	2.35
1	100/107	16.3	29.0	1.78
1	100/104	13.8	19.2	1.39
1	100/102	12.3	14.5	1.18
1	100/102	12.3	14.1	1.15
1	100/100	10.4	9.2	0.88
1	100/100	10.4	8.9	0.86
1	102/100	8.7	6.0	0.69
1	102/100	8.7	5.9	0.68
2	104/100	6.9	3.7	0.54
2	104/100	6.9	3.8	0.55
2	106/100	5.1	1.9	0.37
2	106/100	5.1	2.0	0.39

resistance of the mixture is established by these three constants for all possible conditions. At least three measurements are necessary for a determination, and additional measurements increase the accuracy.

If the rubber compound is used for tire treads, the lower abrasion coefficient S_1 is of primary interest, since the slippage in normal driving ranges from 1 to 2 per cent, and in abrupt starts and braking, from 4 to 5 per cent. It is consequently very important to measure this quantity accurately in the laboratory.

It follows from the preceding that the abrasion characteristics of rubber compounds vary greatly. If it is assumed, for the sake of simplicity, that the breaks in the curves of the two vulcanizates A and B have the same abscissa values, as is often done, then measurements of the upper branch of the curves furnish dependable evidence concerning the abrasion behavior in the lower branch only if the slopes of both branches have changes in the same proportion, that is, if the condition:

$$\frac{(S_1)_A}{(S_1)_B} = \frac{(S_2)_A}{(S_2)_B}$$

is satisfied. Since, as can easily be proved experimentally, this condition is usually not fulfilled, abrasion measurements in the upper branch of the curve

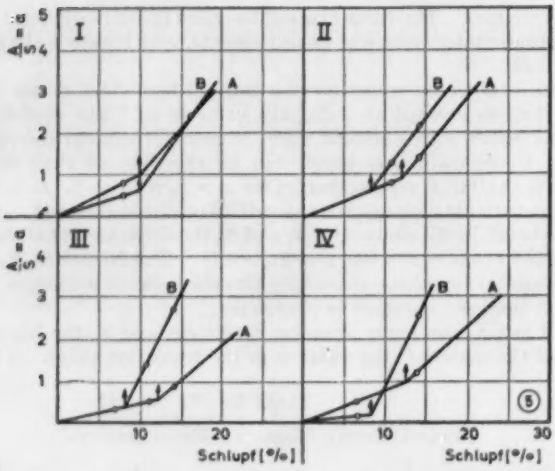


FIG. 5.—Examples of abrasion-slippage characteristics. The abscissa represents the slippage in percentage.

lead, as a rule, to misleading results in any study of tire tread compounds. Finally, if the value x_0 is also varied, complications become even greater. From the graphs in Figure 5, it is seen that, by varying S_1, S_2, and x_0, almost any chance result can be obtained, and any correct results which may be obtained at high degrees of slippage are accidental.

TABLE 3

REDUCED ABRASION VALUES AND QUOTIENTS OF DIFFERENT VULCANIZATES TESTED WITH 10 PER CENT SLIPPAGE

R.P.M.	$\frac{\alpha_{10}}{\text{BL 12}}$	$\frac{\alpha_{10}}{\text{BL 13}}$	$\frac{\alpha_{10}}{\text{BL 14}}$	$\frac{\alpha_{10}}{\text{BL 17}}$	$\frac{\text{BL 13}}{\text{BL 17}}$	$\frac{\text{BL 13}}{\text{BL 14}}$	$\frac{\text{BL 13}}{\text{BL 12}}$
186	1.00	1.56	1.10	0.98	1.59	1.42	1.56
Nürburg value	—	—	—	—	1.58	1.43	1.58

For case I (see Figure 5) some experimental results are given. Table 3 shows the values of α and the quotients for 10 per cent slippage of vulcanizates BL 12, BL 13, BL 14, and BL 17. The quotients in the lower row were calculated from the Nürburg values. The agreement of the experimentally obtained quotients with the Nürburg ratios is very satisfactory in all cases.

In Table 4 the α values and the quotients are given for the same vulcanizates at 24 per cent slippage, with equal surface pressure, and with the same abrasive wheel.

TABLE 4

REDUCED ABRASION VALUES AND QUOTIENTS OF DIFFERENT VULCANIZATES TESTED WITH 24 PER CENT SLIPPAGE

R.P.M.	$\frac{\alpha_{24}}{\text{BL 12}}$	$\frac{\alpha_{24}}{\text{BL 13}}$	$\frac{\alpha_{24}}{\text{BL 14}}$	$\frac{\alpha_{24}}{\text{BL 17}}$	$\frac{\text{BL 13}}{\text{BL 17}}$	$\frac{\text{BL 13}}{\text{BL 14}}$	$\frac{\text{BL 13}}{\text{BL 12}}$
186	4.5	6.0	5.8	4.3	1.39	1.03	1.33
Nürburg value	—	—	—	—	1.58	1.43	1.58

TABLE 5

CONSTANTS OF VULCANIZATES C AND F

Vulcanizate	S_1	S_2	x_0
C	0.64	1.60	12.0
F	0.71	2.46	8.0

The quotients obtained at 24 per cent slippage are very different from those at 10 per cent, and are no longer related to the quotients calculated from the Nürburg values. In particular, vulcanizates BL 13 and BL 14 may be regarded as practically equivalent, and this agrees with the abrasion measurements at 100 per cent slippage.

A good example of cases II and III of Figure 5 is afforded by the vulcanizates designated, for the sake of simplicity, as C and F. Table 5 gives the constants of these vulcanizates.

The characteristic curves for cases II and III, obtained experimentally, are shown in Figure 6. The quotient values for different degrees of slippage recorded in Table 6 were derived from the curves of vulcanizates C and F.

It is then, no longer possible to speak of the quality of a vulcanizate in the foregoing sense, and it would also be meaningless to attempt to make an estimate on the basis of abrasion tests which would correspond to a road test at very high stress (over 10 per cent slippage), where the quotient is different for every value of the slippage. One can merely conclude from this last experiment that the vulcanizate F will behave much worse under high stress than under normal stress.

RESULTS OF POWER CONSUMPTION TESTS

In distinction to the abrasion value, no reduction of the power value is necessarily shown. If the value $L_x - L_0 = L$ is plotted against the slippage as the independent variable, a straight line passing through the origin of the coordi-

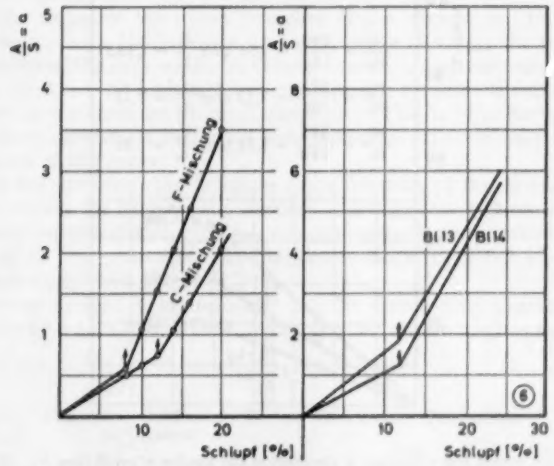


FIG. 6.—Characteristics of mixtures F, C, BL 13, and BL 14. The abscissa represents the slippage in percentage.

TABLE 6

QUOTIENT VALUES OF TWO VULCANIZATES TESTED WITH DIFFERENT DEGREES OF SLIPPAGE

Percentage slippage	$\alpha F/(\alpha C)$	q
8	$\frac{0.570}{0.510}$	1.12
10	$\frac{1.06}{0.64}$	1.65
12	$\frac{1.54}{0.76}$	2.03
14	$\frac{2.03}{1.08}$	1.88
16	$\frac{2.51}{1.40}$	1.80
20	$\frac{3.50}{2.04}$	1.71

nates is obtained, whose direction is constant throughout the range of slippage (for the work curve, see Figure 7).

The power curve can be represented analytically thus:

$L_a - L_0 = \mu \cdot S$ where μ is the proportionality factor. If the value of $\frac{L_a - L_0}{S}$ is plotted against the slippage, as in the case of abrasion, a line parallel to the slippage axis is obtained. Its distance is a measure of the coefficient of friction of the material. This governs the resistance during driving.

$$\frac{L_a - L_0}{S} = \mu = \text{constant}$$

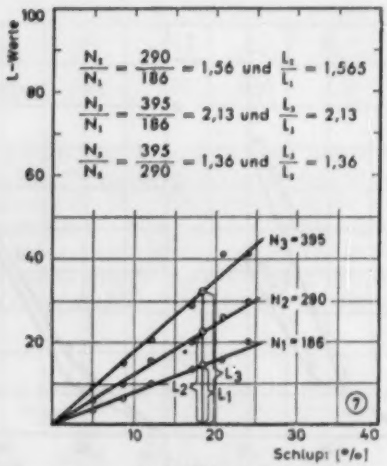


FIG. 7.—Work output L as a function of the slippage and number of revolutions N. (Product BL 17; r.p.m. = 186,290, and 395; $P = 2$.) From the table and curve is derived the equation: $L = \mu \cdot N \cdot S \cdot F(P)$, where μ is the proportionality factor. The abscissa represents the slippage in percentage; the ordinate the L value.

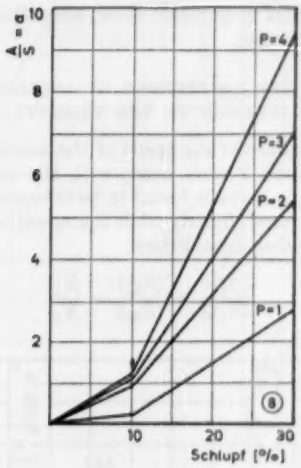


FIG. 8.—Characteristics of a product as a function of the surface pressure P. (r.p.m. = 182; mixture S; Redurit abrasive wheel.) The abscissa represents the slippage in percentage.

DEPENDENCE OF THE COEFFICIENT OF ABRASION AND WORK OF ABRASION ON THE PRESSURE

In order to study the relation of abrasion to pressure, the dynamometer force was varied from 1 to 4 kg., and the corresponding abrasion-slippage graphs were constructed. The position of the break in the curves is, within the limits of experimental error, independent of the surface pressure, i.e., of load P (see Figure 8). In the increase of the slope angle, the two branches of the curve are different, as Table 7 shows.

While the slopes of the upper branches of the curves, i.e., the S_2 values, increase linearly with the pressure up to pressures of 4 kg., the slopes of the lower branches of the curves, the S_1 values, approach limiting values at 2–3 kg. (Figures 9, 10, 11). At high surface pressures, the abrasion therefore becomes independent of the pressure at small slippages. This is of importance experimentally, since agreement with road tests would be expected only for the proportional part of the curve.

As with the abrasion, the L values are a function of the surface pressure. The power values for 24 per cent slippage and r.p.m. = 182 were chosen for this graphical representation. The L values increase linearly with the pressure in the range of low pressures. At higher pressures, they fall along a curve which is convex upward (Figure 12).

The curves derived experimentally can be represented analytically very satisfactorily by a parabola of the form: $y = \alpha \cdot P^n$, where n is less than 1. The

TABLE 7

ABRASION COEFFICIENTS FOR DIFFERENT PRESSURES

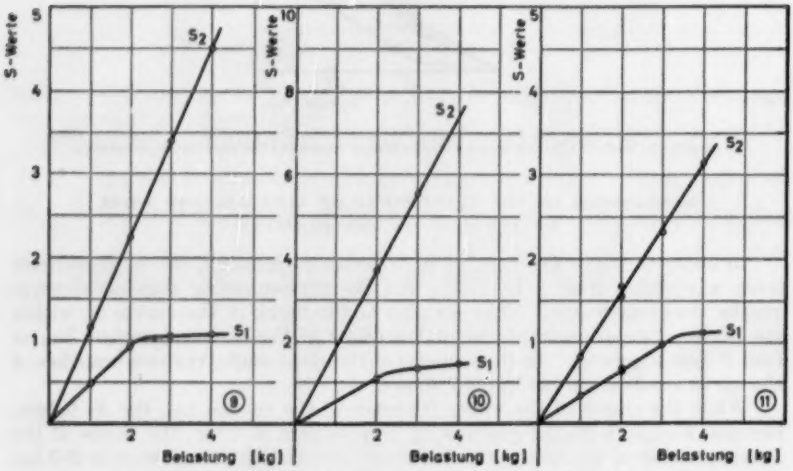
	P=1	P=2	P=3	P=4
S_1	0.48	0.96	1.05	1.08
S_2	1.16	2.24	3.48	4.48

power values and coefficient of abrasion show, accordingly, different characteristics under different pressures.

RELATION OF THE COEFFICIENT OF ABRASION AND WORK OF ABRASION TO THE VELOCITY

In a study of the influence of the speed of the machine on the abrasion and power values, speeds 1 and 2 were used, with the pressure the same. The position of the break in the curve is found to be independent of the speed of the machine. S_1 and S_2 increase linearly with the speed, as is seen from Table 8. The following relation is thus established:

$$\frac{(S_1)1}{(S_1)2} = \frac{(S_2)1}{(S_2)2} = \frac{N_1}{N_2}$$



FIGS. 9, 10, and 11.—The S_1 and S_2 abrasion coefficients as functions of the pressure. FIG. 9. Vulcanizate S; r.p.m. = 182; Redurit wheel. FIG. 10. Vulcanizate S; r.p.m. = 272; Redurit wheel. FIG. 11. Vulcanizate C; r.p.m. = 182; Redurit wheel. The abscissae represent the load in kg.; the ordinates the S values.

The work of abrasion is a linear function of the speed, as is also the rate of abrasion (see Figures 7 and 13), so that the following equation holds true for constant surface pressure:

$$\frac{L_1}{L_2} = \frac{N_1}{N_2}$$

With respect to the work of abrasion, but not to the abrasion value, the speed and slippage are, therefore, equivalent.

DEPENDENCE OF THE ABRASION ON THE CHARACTER OF THE ABRASIVE SURFACE

In a study of the dependence of the abrasion on the material of the abrasive wheel, three vulcanizates (C, F, and F-S), whose rating was known from road

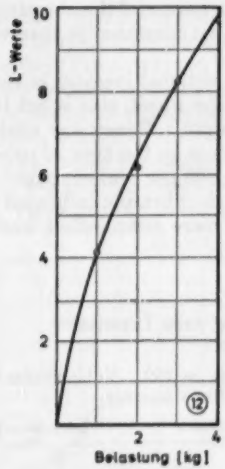


FIG. 12.—Work values for 24 per cent slippage and variable pressure. (r.p.m. = 182; mixture 8; Redurit wheel.) The abscissas represent the load in kg.; the ordinates the L values.

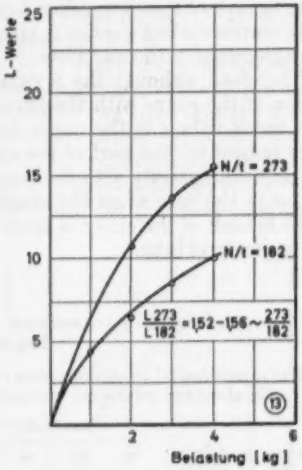


FIG 13.—Work values for 24 per cent slippage as a function of pressure and speed of machine. (r.p.m. =182. and 273; mixture 8; Redurit wheel.) The abscissas represent the load in kg.; the ordinates the L values.

tests, were abraded on five different abrasive wheels under standard experimental conditions (P = 2, r.p.m. = 182). These were:

1. A Redurit wheel.
2. A Dirubin alpha wheel.
3. An iron wheel covered with 150-grain silicon carbide paper.
4. An iron wheel covered with 100-grain silicon carbide paper.
5. An iron wheel covered with 120-grain aluminum oxide paper.

The diameter of the wheels was in all cases between 113.5 and 113.9 mm. The experimental results are summarized in Table 9, including the two coefficients of abrasion S_1 and S_2, the position x_0 of the transition point, and the work of friction L. It is seen that the absolute abrasion values depend greatly on the quality of the abrasive surface. The papers were much more severe than the smooth polished stone, while aluminum oxide paper was more abrasive than silicon carbide paper of the same grain. If the quotients F/C and (F-S)/C are calculated for the S_1 values, they are found to be surprisingly constant; their absolute values agree quite well with values obtained in road tests. We thus arrive at the simple fact that a laboratory evaluation, if restricted to the

TABLE 8

ABRASION COEFFICIENTS WITH DIFFERENT SPEEDS OF THE MACHINE

Number N of revolutions per min.	$S_1(P=1)$	$S_1(P=2)$	$S_2(P=1)$	$S_2(P=2)$
182	0.42	0.82	1.20	2.50
273	0.68	1.24	1.83	3.66
q	1.58	1.51	1.53	1.47

lower branch of the curve, does not depend on the nature of the abrasive wheel. If the corresponding quotients are derived for S_2, no constancy is observed, nor any agreement with road tests.

Therefore, although the S values show a proportional increase in the lower section of the curve with the abrasive power of the wheel, this is not the case with the S values in the upper branch of the curve. Hence any evaluation, when judged by this part of the curve, still depends on the type of paper, and this accords perfectly with the result obtained at 100 per cent slippage. Here, too, as in the case when the pressure is varied, the abrasion indicated by the upper branch of the curve is governed by other, more complicated, and as yet not understood laws.

TABLE 9

RESULTS OF ABRASION MEASUREMENTS WITH DIFFERENT ABRASION MATERIALS

The experimental conditions were: $P = 2$ kg.; r.p.m. = 182. Vulcanizates C and F were natural-rubber mixtures; vulcanizate F-S was a Buna mixture.

	Vulcanizate C				Vulcanizate F				Vulcanizate F-S			
Abrasive wheel	S_1	S_2	x_0	L	S_1	S_2	x_0	L	S_1	S_2	x_0	L
Redurit	0.64	1.65	12.0	7.2	0.71	2.46	8.0	7.3	0.82	2.30	11.5	7.2
Dirubin-alpha	0.61	1.60	12.1	7.1	—	—	—	—	0.78	2.10	11.5	7.2
Silicon carbide paper (150 grain)	1.06	3.08	9.1	5.7	1.18	3.98	5.7	5.8	1.36	2.92	8.7	5.8
Silicon carbide paper (100 grain)	1.24	3.76	8.9	6.0	1.40	5.60	6.4	5.8	1.56	4.05	10.1	5.9
Corundum paper (120 grain)	1.48	3.96	7.4	5.0	1.68	6.80	6.4	5.4	1.87	4.40	7.8	4.2

TABLE 9 (continued)

Abrasive wheel	$\left(\frac{F}{C}\right)_{S_1}$	$\left(\frac{F\text{-}S}{C}\right)_{S_1}$	$\left(\frac{F}{C}\right)_{S_2}$	$\left(\frac{F\text{-}S}{C}\right)_{S_2}$
Redurit	1.11	1.28	1.49	1.39
Dirubin-alpha	—	1.28	—	1.31
Silicon carbide paper (150 grain)	1.11	1.28	1.29	0.95
Silicon carbide paper (100 grain)	1.13	1.26	1.49	1.08
Corundum paper (120 grain)	1.135	1.26	1.72	1.11
Nürburg value	1.11	1.24		

The cause of the non-proportional increase of S_2 should be sought:

(1) in the very different positions of the transition point x_0; and
(2) in the different hardnesses of products, which undoubtedly influence the abrasion measurement at high slippages on the gritty surfaces.

That the abrasion process is entirely different in the case of paper is also evident from the sharp drop of the L values from 7.2 to about 5.2, at the same time that the abrasion values increase. Because of the complex nature of L, which comprises the work of friction and the work of attrition, no definite conclusions about its significance can be drawn.

For the sake of completeness, a few measurements were made at various pressures with the corundum paper wheel. The experimental material was

vulcanizate C, which was also tested under the same conditions with the Redurit wheel. The results are shown in Figures 14 and 15.

Here too (Figure 14), an increase of S_1 and S_2 proportional to the surface pressure is evident; but with the distinction that the limiting value of the lower branch of the curve is practically reached at a load of 2 kg., and that the S value of the upper branch of the curve also approaches a limiting value very rapidly at 2 to 3 kg., while the Redurit wheel shows a strict proportionality up to 4 kg. Probably this phenomenon bears some relation to the crystalline structure of the surface, whose cutting action is limited by the size of the grains, so that an in-

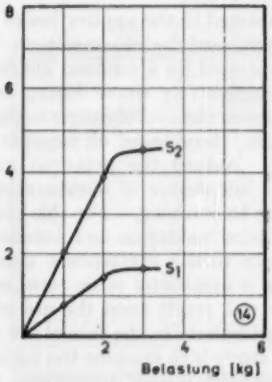


FIG. 14.—Dependence of the abrasion coefficient on the pressure. (r.p.m. = 182; mixture C; corundum paper wheel.) The abscissa represents the load in kg.; the ordinate the S value.

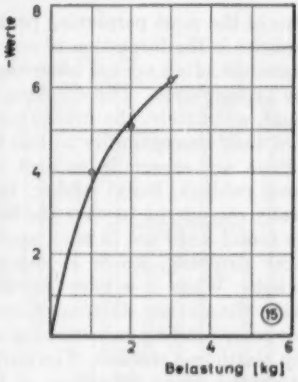


FIG. 15.—Work values for 24 per cent slippage as a function of the pressure. (r.p.m. = 192; mixture C; corundum paper wheel.) The abscissa represents the load in kg.; the ordinate the S value.

crease of pressure causes little increase of abrasion. The phenomenon was not investigated further, however. The experiments show that, at small and medium pressures, the same laws are valid as for a smooth wheel. This is further confirmation of the correctness, in principle, of the method. The L curve is parabolic, as with a smooth wheel (Figure 15).

Most of the results of the studies of the influence of various factors involved in the composition of compounds and operating conditions were lost because of the War. Hence it is impossible to discuss these in detail. Let it merely be noted that a natural-rubber compound which would normally be regarded as undercured, and which was developed systematically with the aid of the machine, showed surprising results in Nürburg tests.

OZONE RESISTANCE OF BUTYL VULCANIZATES *

D. C. Edwards and E. B. Storey

Polymer Corporation, Ltd., Sarnia, Ontario

INTRODUCTION

One of the most perplexing problems encountered in the application of rubber articles is the formation of cracks in the surface of the vulcanizates. This phenomenon often occurs when the article is exposed, in a strained condition, to the atmosphere. The cracking becomes progressively worse during exposure, and, ultimately, the rubber part may fail in service. Polymeric materials vary in their susceptibility to this type of attack; those based on isoprene and butadiene are especially subject to cracking. Among the principal manufactured rubbers, Butyl rubber, because of its low degree of unsaturation, is generally considered to offer the best resistance to cracking. For this reason, it has found wide use in such applications as wire insulation and automotive weather stripping, where exposure under strain to the atmosphere must be tolerated. While it is true that Butyl rubber is inherently more resistant to cracking than other elastomers, cracking may still result from the use of improper compounding or processing methods, particularly in the case of low cost, highly plasticized stocks. The purpose of this study is to examine the variables affecting the ozone resistance of Butyl rubber, and, hence, to develop compounding principles suited to the preparation of economical weather resistant products.

TEST APPARATUS

The vulcanizates were tested in an ozonizer modified from the Bush Ozonator and the apparatus is shown in Figure 1. The air-flow through the test chamber was maintained at 2 cu. m. per hour, with an ozone concentration of 25 parts per 100 million parts by volume of air, and at a temperature of 120° F. The air from a 20 lb. per sq. in. supply was divided into two streams, and the flow was regulated by a pressure reducing valve, 1, inserted in each line. The volume flow of air was measured by 2L-15 rotameters, 2.

The air passed up two columns, 3, containing granular soda-lime, where objectionable impurities were removed prior to entry into the test chamber. One stream of air passed around a shielded 750-volt mercury-vapor lamp, shown at 4. The concentration of ozone was adjusted by varying the voltage applied to lamp with a Variac. The two streams of air were united to give the desired ozone concentration and volume flow of air before entry into the test chamber. The ozonized air entered the chamber below the perforated floor, 6, and was heated to 120° F in the chamber by means of resistance wire wound around the exterior of the chamber. The temperature of the air in the chamber was controlled by a bimetallic thermoregulator located above the sample rack. The air was removed from the chamber by a vacuum line fitted loosely over the

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 31, No. 2, pages 45–69, April 1955. This paper was presented before the Rubber Chemistry Division of the Chemical Institute of Canada, June 1954, and before the Manchester Section of the Institution of the Rubber Industry, Manchester, England, March 21, 1955.

outlet at 8. The residual ozone in the air was decomposed by passing the air over granular soda-lime.

The concentration of ozone in the test chamber was determined by the method of Crabtree and Kemp[1]. The ozonized air was withdrawn from the test chamber through a perforated sampling tube, 5, located below the sample rack. It was mixed with a buffered 20 per cent solution of potassium iodide and passed through a spray nozzle, whereupon the ozone was absorbed and iodine liberated from the potassium iodide. The sample of 0.25 cu. m. of air was measured with a rotameter and was collected over the course of 1 hour.

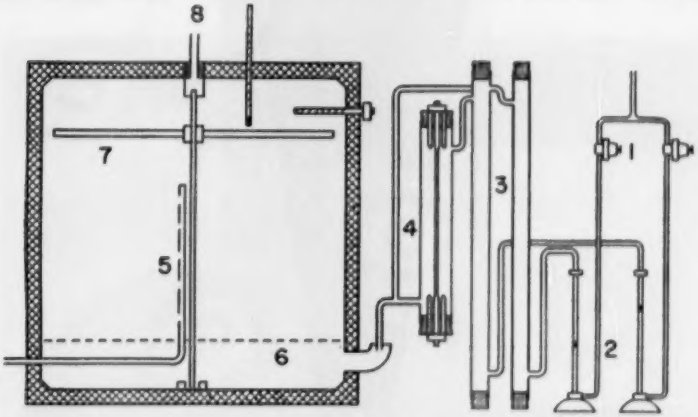


FIG. 1.—Ozoniser apparatus. Schematic drawing.

The liberated iodine was titrated amperometrically with 0.001 *N* sodium thiosulfate using the dead-stop method of Foulk and Bowden[2].

TRAPEZOIDAL SPECIMEN

A trapezoidal specimen was employed to determine the influence of strain on ozone cracking. This specimen was cut from a standard test sheet $\frac{3}{32}$ inch thick, to give a test-section 4 inches in length, tapering from a 2-inch width at one end to a $\frac{1}{4}$-inch length at the opposite end. The ends of the specimen were enlarged to provide a clamping surface. The mounted test-specimen is shown in Figure 2. The specimen was mounted in a rack and elongated until the length of the 4-inch section had been increased to 5 inches. After exposure for the desired time in the ozonizer, a $\frac{1}{4}$-inch wide strip was cut from the central portion of the 4-inch test length, and a line was drawn with white ink down the center of this strip. The strip was stretched to enlarge the cracks in the speci-

men, and the number of cracks was counted with a microscope, at 60 magnifications, over each successive ¼-inch length of the strip.

The strain in the specimen during exposure to ozonized air was determined for each vulcanizate. A 6 × ¼-inch specimen was suspended from a clamp and loads were applied by successive additions of mercury to a bottle attached to the opposite end of the strip. The elongation at each load was measured with

FIG. 2.—Trapezoidal specimen.

a cathetometer after 1 minute under each load. The load required to elongate the trapezoidal specimen from 4 to 5 inches was determined in a similar manner. In this way, the average strain could be calculated for each ¼-inch length of the trapezoidal specimen.

TRIANGULAR SPECIMEN

The triangular test-specimen[3] and the method of mounting are shown in Figure 3. The compounded stock was extruded through a triangular die with a

½ Royle extruder, to give an extruded section with a slightly larger cross-sectional area than that of the desired specimen. The extruded strip was vulcanized in a flash-type mold to give a triangular cross-section with a base width of ¾ inch and a height of ½ inch. The length of the specimen was 12 inches. Two marks were placed on the specimen, 7½ inches apart and centrally located between the ends of the specimen. The ends of the specimen were bound together at these marks with aluminum wire, to give a sliding fit on a 51-mm. glass tube. A number of test-specimens were mounted, side by side, on a 10-inch length of glass tube. The prepared specimens were covered with a paper bag and allowed to rest for 48 hours at room temperature. The glass tube was placed,

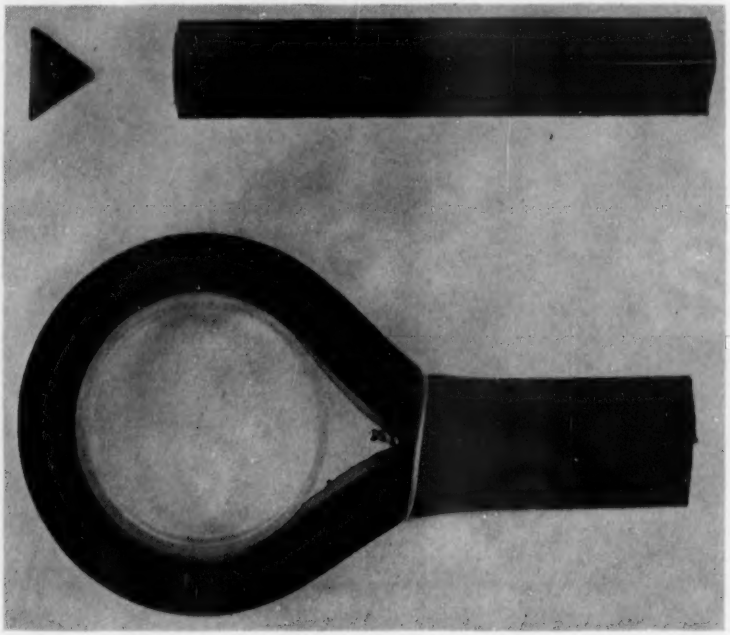


FIG. 3.—Triangular specimen.

then, on the sample rack, 7, in the chamber of the ozonizer. The samples were examined periodically until cracks of suitable depth had formed on the edge of the triangular specimen. The samples were removed from the test chamber, and the number and depth of cracks were measured by the method described below.

OUTDOOR TESTS

The triangular specimens were mounted on aluminum tubes, 2 inches in outside diameter, having been tied in loops as described above. The mandrels were placed on a wooden frame, about 5 feet above the ground, so that the apex of the triangular specimen faced due south, and the test area was that portion of the specimen that was inclined at an angle of 45° to the horizon.

RATING METHOD

There have been many methods of rating the severity of ozone cracking proposed by investigators in this field of rubber technology; some are based on visual ratings, some on the number or the dimensions of the cracks, and some on the mechanical or electrical behavior of the cracked specimen. In the present work, a rating method was developed that was based, primarily, on the appearance of the vulcanizate, but whose evaluation depended on a measurement of the number and depth of cracks in the surface of the vulcanizate.

TABLE I

Sample	Visual score	N_D	D	$\epsilon N_D D$	$\sqrt[3]{N_D D^2}$	$\sqrt[3]{\epsilon N_D D^2}$	$\sqrt[4]{\epsilon N_D D^3}$
C	149	10	16	160	50.6	34.5	28.5
G	129	45 2 1	6 14 15	313	47.3	26.5	20.8
I	123	8 1 1 1 1	7 8 10 15 16	105	32.2	22.7	19.7
D	98	7 3 2	3 4 16	65	25.0	20.4	19.1
A	88	51 1 1	3 14 15	182	29.6	19.6	17.5
F	77	2 8 3	4 5 11	81	24.4	17.2	14.9
H	57	8 1 1	6 7 8	63	20.0	13.7	11.4
J	41	28 1 2	3 6 8	106	20.4	12.6	10.4
B	33	43 17	2 3	137	18.0	9.3	6.7
E	30	10	4	40	12.6	8.6	7.1

Ten artificially cracked specimens were prepared by placing razor cuts of varying numbers and depths along the apex of the triangular test-specimens. The specimens were mounted in random order on a mandrel. Fifteen observers were asked to list the specimens in what they considered to be the order of decreasing severity of cracking. The specimen heading each list was given a score of ten, the next specimen nine, and so on down to one for the specimen deemed to show the least severe cracking. The scores for each specimen were then totalled, and a correlation was sought between the order of the visual scores and the measured depths and the numbers of the cuts. It was to be expected that considerable weight must be given to depth, compared to number.

As a convenient means of doing this, consideration was given to expressions of the form $\epsilon N_D D^n$, where N_D is the number of cracks of depth D per unit length of the specimen. A suitable value for D was estimated by trial and error, as shown in Table 1. The nth root is employed in order that the result may be expressed in convenient numbers.

It may be seen from Table 1 that the square gives too little weight to the depth (compare samples D and A), while the fourth power tends to weight the depth too heavily (samples B and E). The cube function ranks the samples in the same order as the visual score, and was, therefore, chosen as a suitable

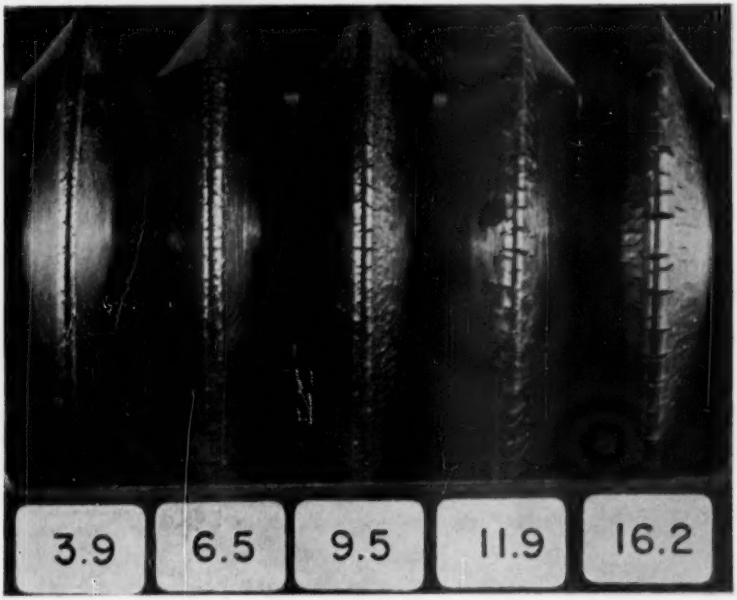


FIG. 4.

expression for use in this work. The coefficient of correlation between the visual score and the cube function is 0.97.

In the application of this rating procedure, the triangular specimens were exposed until cracks were produced along the apex of the triangle that were more than 0.005 inch deep. The depths of the cracks were measured with a brass disk 1½ inches in diameter and 0.01 inch thick. This disk was graduated by placing marks on the surface of the disk, at intervals around its circumference, to indicate the distance from the edge of the disk in increments of 0.01 inch. The graduations on this depth gauge ran from 0 to 24, or from 0 to 0.24 inch in depth. In making a measurement, a 2-inch length was measured off along the outer periphery of the triangular specimen, midway between the ends of the specimen. The depth of each crack along this 2-inch portion was measured

with the depth gauge, but cracks of less than 0.005 inch were ignored in the test. The rating for the specimen was calculated from the expression:

$$\text{Rating} = \sqrt[3]{\epsilon N_D D^3}$$

where N_D is the number of cracks of depth D (in one-hundredths of an inch), per 2-inch length of specimen.

This rating value and the appearance of the vulcanizate may be compared in Figure 4, where five vulcanizates are shown with different degrees of ozone cracking.

The relationship between the rating value and the time of exposure in the ozonizer was found to be linear, as illustrated in Figure 5. Each of these vulcanizates was exposed to ozone, and the rating value was measured at various periods during the test.

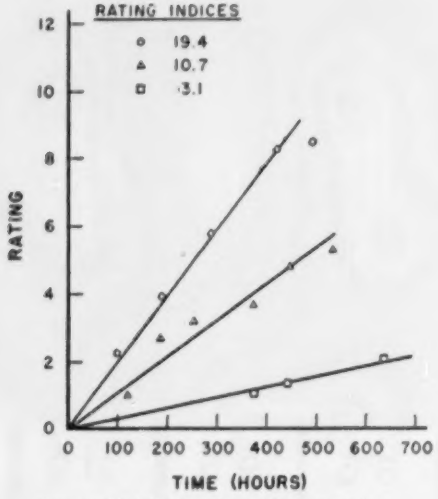


FIG. 5.—Variation in rating with exposure time.

A sample of the control compound was included in each test run. From a number of tests, it was found that the rating of the control specimen increased, on the average, by one unit per 100 hours' exposure in the ozonizer. The control compound was, therefore, useful as a supplementary check on the condition of ozone concentration and temperature in each test. The rating of the control compound after 1000 hours of exposure was defined as the *rating index* of that compound. In determining the rating index of an experimental compound, the rating value was measured after a convenient time of exposure, calculated as a rating per 1,000 hours, and adjusted for the observed rating value of the control specimen in the same test run. That is:

$$\text{Rating index} = \frac{X}{C} \times 10$$

where X is the rating value of the experimental specimen and C is the rating value of the control specimen.

TEST RECIPES

CONTROL COMPOUND

Polysar Butyl 400	100
EPC black	50
Zinc oxide	5
Stearic acid	3
Benzothiazolyl disulfide	0.5
Tetramethylthiuram disulfide	1
Sulfur	2
Cure at 307° F, 20 minutes	

The experimental test recipes are shown in the tables.

COMPOUNDING PROCEDURES

The control compound was mixed on a 6 × 12 inch mill using a 400-gram mix, and following the compounding procedure outlined in the "Specifications for Government Synthetic Rubbers"[4].

The Banbury mixes were prepared in a Type B Banbury mixer. In general, a 1000 cc. batch was prepared, using a rotor speed of 77 r.p.m. with the rotor and gates at a starting temperature of 210° to 220° F.

RESULTS

OZONIZER TESTS

It has been well established that the surface cracking of a vulcanizate by ozone depends on the presence of mechanical strain in the surface. Indeed, the number and depth of the cracks will vary with strain present in the vulcanizate. The trapezoidal specimen shown in Figure 2 illustrates this effect. Here, the strain varied from about 8 per cent at the wide end to about 80 per cent at the narrow section. At low strains a few deep cracks were formed in the vulcanizate. The number of cracks increased, and their size decreased, as the strain progressively increased to a maximum at the narrowest section of the specimen.

The effects of the chemical composition of the elastomer and the mechanical strain in the surface must be combined in considering the effect of ozone attack on a rubber article. Their combined action has led to the concept of a threshold strain for the formation of surface cracking. Below this threshold strain, no cracks are formed in the surface, even over extended periods of time. The number of cracks increases very rapidly above this threshold strain. The chemical composition of the elastomer has the predominant effect in determining the threshold strain, while the magnitude of the strain has the predominant effect in determining the number of cracks formed at strains above the threshold strain.

These effects were examined for a number of elastomers by exposing trapezoidal specimens to an atmosphere containing 25 parts of ozone per 100 million parts by volume of air. The test recipes are given in Table 2, and the relationships between the number of cracks formed and the strain in the vulcanizates are shown in Figure 6.

The threshold strain for the natural rubber, the butadiene acrylonitrile copolymer (Polysar N-301), and the various butadiene styrene copolymers was about constant, namely 7–9 per cent. The threshold strain for the chlorobutadiene polymer was about 18 per cent, and that for the isobutylene isoprene copolymer (Polysar Butyl 200) was the highest for the elastomers studied, at

TABLE 2

NUMBER OF CRACKS VS. ELONGATION

Polymer	Test recipes						
	Polysar Butyl 200	Polysar S-50	Polysar Krynol	Polysar Krylene NS	Polysar N-301	Neoprene Type W	Smoked sheet
Polymer	100	100	100	100	100	100	100
FEF black	49	48	48	48	47	36	49
Stearic acid	1	1	1	1	1	1	1
Magnesia (light calcined)	4	4	4	4	4	4	4
Zinc oxide	5	5	5	5	5	5	5
Tetramethylthiuram disulfide	0.75	—	—	—	—	—	—
Selenium diethyldithiocarbamate	0.75	—	—	—	—	—	—
Ethylene thiourea (2-mercaptoimidazoline)	—	—	—	—	—	0.5	—
Mercaptobenzothiazole	0.5	1.5	1.5	1.5	1.5	—	0.8
Diphenylguanidine	—	1	1	1	—	—	0.1
Sulfur	1.5	2	2	2	2	1	2.75
Cure at 292° F (minutes)	35	20	20	20	25	35	15
Hardness (Shore type A-2)	59	62	51	59	60	57	58
Modulus at 100% (lb. per sq. in.)	285	775	580	635	550	535	465
Tensile strength (lb. per sq. in.)	1830	2410	2015	2890	3170	3280	2690
Elongation at break (%)	665	220	260	335	400	370	390
Exposure time in ozonizer (hours)	90	40	40	40	45	100	40

about 26 per cent. These data show that the range of strains encountered in service may be increased without ozone cracking if the elastomer has a low degree of unsaturation (Polysar Butyl 200). The presence of certain chemical groups in the butadiene molecule also increases the threshold strain. Thus, the presence of the chlorine atom in the chloroprene molecule provides a significant increase in the threshold strain, while the presence of either a methyl group (natural rubber) or a styrene group (Polysar S-50 or Polysar Krylene NS) resulted in a lower threshold strain. It is noteworthy that the oil-enriched butadiene styrene copolymer (Polysar Krynol) had about the same threshold strain as that of Polysar S-50.

In the present tests, the temperature and ozone concentration have been held constant at 120° F and 25 parts per 100 million parts by volume of air.

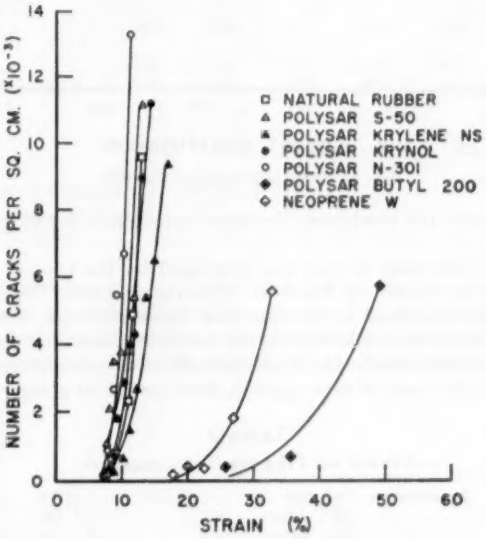


FIG. 6.—Variation in number of cracks with strain.

It would be expected that an increase of either the temperature or the ozone concentration would increase the formation of cracks in the vulcanizate, as has been reported in the literature[5]. These conditions, however, result in a more rapid and extensive degree of cracking than is normally encountered in outdoor exposure. The rather high level of strain provided by the triangular specimen, namely 25 per cent, is well suited to the study of Butyl rubber compounds.

The effect of the unsaturation of Butyl polymers on the rating index was determined for a channel black recipe. The data are shown in Figure 7 and Table 3. The rating index and the number of cracks increased as the unsaturation, due to the isoprene content of this copolymer, increased from 0.7 to 2.2 mole-per cent. The effect of the unsaturation of the polymer on the ozone cracking is a chemical one. It may be assumed that the attack by an ozone molecule on the chain segment containing a double bond produces scission of the chain element and, hence, a nucleus for an ozone crack. Hence, the greater

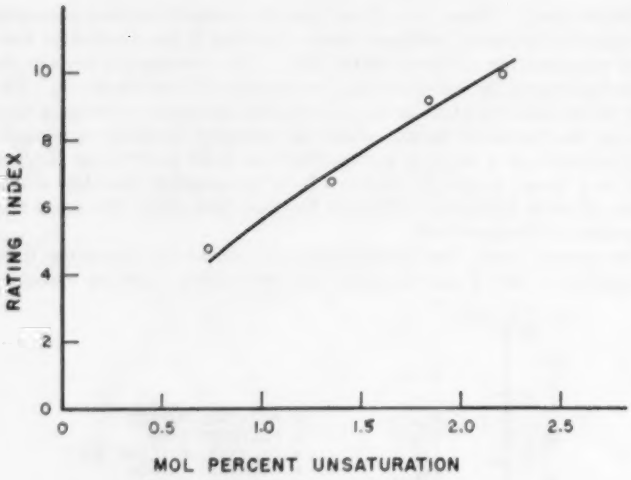


FIG. 7.—Effect of polymer unsaturation.

the unsaturation of the elastomer, the more susceptible it will be to attack by ozone.

The effect of the state of cure was examined for the typical Polysar Butyl weatherstrip recipe shown in Table 4. The rating index (Figure 8) and the number of cracks decreased as the cure time increased from 15 to 100 minutes at 292° F. An increase of the state of cure would reduce the number of double bonds in the elastomer chain that might be subject to ozone attack. The effect of an increase in the state of cure appears, however, to be greater than could be

TABLE 3

EFFECT OF POLYMER UNSATURATION

Base recipe:	Polymer	100
	EPC black	50
	Zinc oxide	5
	Stearic acid	3
	Benzothiazolyl disulfide	0.5
	Tetramethylthiuram dislufide	1
	Sulfur	2
	Cure at 307° F ,20 minutes	

	PB-100	PB-200	PB-300	PB-400
Mole-per cent unsaturation	0.73	1.35	1.83	2.20
Hardness (Shore type A-2)	40	48	51	55
Modulus at 400% (lb. per sq. in.)	335	755	1000	1030
Tensile strength (lb. per sq. in.)	—	2860	2850	2730
Elongation at break (%)	1010	820	755	730
Ozonizer test				
Rating index	4.8	6.8	9.2	10
Outdoor exposure (test started July 1, 1952)				
(1) First crack (days)	166	180	96	124
(2) Rating (620 days)	<1	<1	<1	<1

TABLE 4

EFFECT OF STATE OF CURE

Base recipe:	
Polysar Butyl 301	100
FEF black	63
Mineral oil plasticizer	25
Zinc oxide	4
Magnesia (light calcined)	4
Stearic acid	1.5
Petrolatum	3
Mercaptobenzothiazole	0.5
Tetramethylthiuram disulfide	0.75
Selenium dimethyldithiocarbamate	1
Sulfur	1.5

Cure at 292° F (min.)	15	20	25	35	50	70	100
Hardness (Shore type A-2)	44	46	47	49	50	52	52
Modulus at 400% (lb. per sq. in.)	480	550	635	705	780	835	885
Tensile strength (lb. per sq. in.)	1720	1755	1745	1745	1665	1680	1705
Elongation at break (%)	760	730	700	670	610	580	560
Ozonizer test							
Rating index	17.5	13.5	11.9	11.1	9.1	5.7	3.8
Outdoor exposure (test started October 29, 1953)							
(1) First crack (days)	—	—	—	—	—	—	—
(2) Rating (150 days)	0	0	0	0	0	0	0

explained on this basis. It is suggested that the presence of cross-links between adjacent polymer chains distributes the concentration of stress that would occur by the scission of a polymer chain throughout the vulcanizate. This effect would reduce the strain in any one polymer chain and, therefore, the possibility

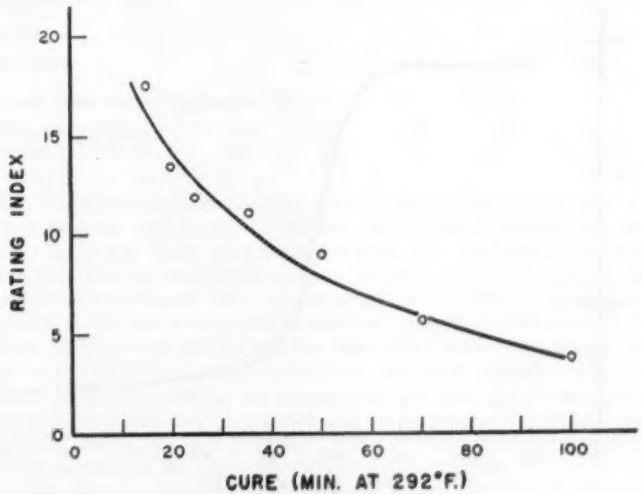


FIG. 8.—Effect of cure time.

TABLE 5

EFFECT OF CARBON BLACK LOADING

Base recipe:					
Polysar Butyl 301	100				
Zinc oxide	5				
Stearic acid	3				
Benzothiazolyl disulfide	0.5				
Tetramethylthiuram disulfide	1				
Sulfur	2				
FEF black (PHR)	10	30	50	70	90
Cure at 307° F (min.)	12	13	17.5	40	70
Hardness (Shore Type A-2)	29	41	55	72	81
Modulus at 300% (lb. per sq. in.)	200	510	1005	1640	—
Tensile strength (lb. per sq. in.)	2950	2700	2015	1695	1625
Elongation at break (%)	830	770	610	340	195
Ozonizer test					
Rating index	14.0	14.0	3.2	2.2	less than 1
Outdoor exposure (test started April 14, 1953)					
(1) First crack (days)	77	77	140	140	140
(2) Rating (330 days)	3.4	2.7	<1	<1	<1

of attack by ozone. Whatever may be the mechanism of this action, it should be emphasized that a high state of cure was the most effective factor found in this work to reduce ozone cracking.

The effect of carbon black loading on the ozone resistance of a Polysar Butyl 301 recipe is given in Table 5 and Figure 9. The rating index decreased rapidly between loadings of 30 and 50 PHR of FEF black, and there was a slight decrease in ozone cracking for higher loadings of carbon black. The action of

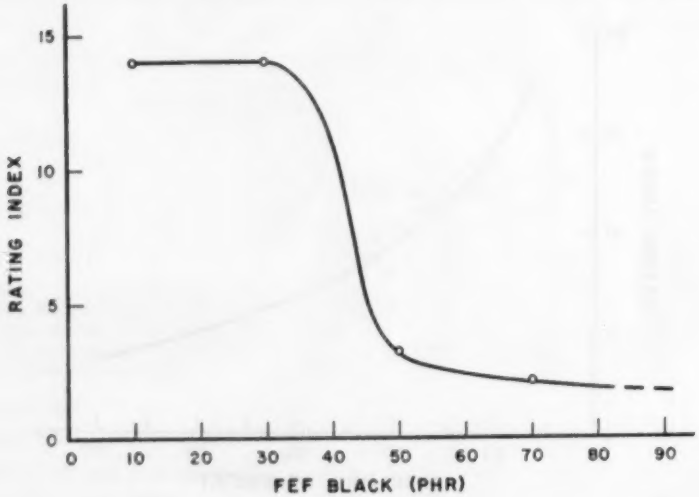


FIG. 9.—Effect of black loading.

carbon black may be interpreted as a reinforcement of the vulcanizate network similar to that obtained by sulfur cross-linkages. It should be noted that in this instance the effect of the state of cure was minimized by selecting comparative states of cure at the various carbon black loadings. For this purpose, comparative states of cure of Polysar Butyl vulcanizates were defined as the cure time required to give a constant ratio of the actual modulus to the maximum modulus that could be obtained over an extended range of cure times. In subsequent tests, the specimens were purposely compared at a low state of cure, in order to obtain comparative results in a reasonably short period of exposure.

Regarding the type of carbon black, the finer particle size blacks show a decided superiority over the coarser blacks when compared at equivalent states of cure. FEF black appears to offer the best balance of properties with respect to processing properties, rate of cure, and ozone resistance.

TABLE 6

EFFECT OF OIL LOADING

Base recipe:	Polysar Butyl 301	100
	EPC black	50
	Zinc oxide	5
	Stearic acid	3
	Benzothiazolyl disulfide	0.5
	Tetramethylthiuram disulfide	1
	Sulfur	2
	Cure at 307° F, 40 minutes	

Mineral oil Plasticizer (PHR)	0	5	10	15	20	25
Hardness (Shore Type A-2)	52	46	44	41	40	34
Modulus at 400% (lb. per sq. in.)	1340	1055	925	770	665	535
Tensile strength (lb. per sq. in.)	2780	2770	2820	2630	2390	2070
Elongation at break (%)	630	680	720	750	770	770
Ozonizer test						
Rating index	2.0	6.0	9.6	12.1	15.2	19.8
Outdoor test (test started September 2, 1952)						
(1) First crack (days)	44	44	44	44	44	44
(2) Rating (470 days)	<1	<1	<1	<1	4.0	4.9

So far, we have examined variables that might be expected to give a highly reinforced network and hence, to reduce the effect of scission by an ozone molecule. In Table 6 are shown data for various loadings of a mineral oil plasticizer in a Polysar Butyl 301 recipe. It will be seen in Figure 10 that the rating index varied directly with the loading of oil. While it is usually necessary to add a plasticizer to any elastomeric compound to facilitate the processing operations, an increased mobility of the compound results in a greater freedom of action of the individual polymer chains. Any one polymer chain would be more likely to be attacked by an ozone molecule, and the severed chain segments would be reinforced to a lesser degree by the sulfur cross-linkages or carbon black bonds. Such a network theory of reinforcement of the polymer chains is in agreement with the experimental observations.

Since the plasticizer efficiency of various softeners for a particular polymer may be different, the effect of different plasticizer types was examined for a

Polysar Butyl 301 recipe. A comparison of mineral oil plasticizers of similar physical properties, but varying as to aromatic, naphthenic, and paraffinic content, showed no significant differences. A liquid polybutene plasticizer and a viscous cumaroneindene resin imparted relatively poor ozone resistance, while an ester plasticizer, dioctyl phthalate, and a liquid furane polymer, gave low rating indices in the ozonizer tests. Plasticizers of the coal-tar type were found to perform exceptionally well, but it should be noted that a careful selection is necessary in considering this class of materials. Many tend to retard the vulcanization of Butyl compounds, and are objectionable in some applications because of odor and discoloration. However, refined coal-tar products are available that appear satisfactory in all of these respects, while still conferring improved resistance to ozone.

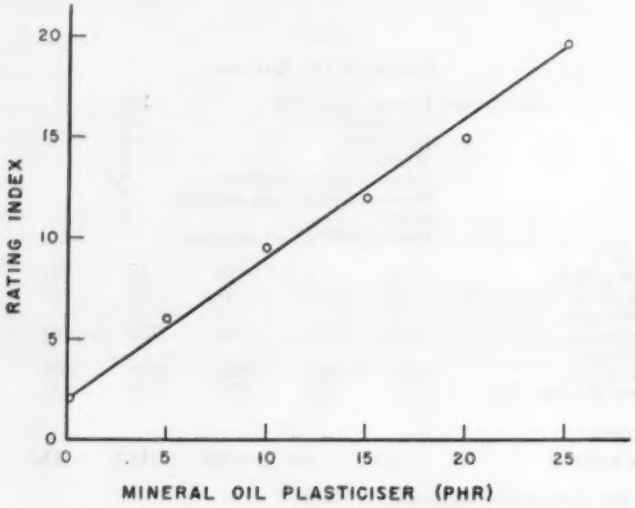


FIG. 10.—Effect of plasticizer loading.

Ozone cracking has been considered as an oxidative phenomenon, and much experimental work has involved the examination of various antioxidants. Since ozone attack occurs at the surface of the vulcanizate, any means of protecting the surface should be effective in reducing ozone cracking. One of the most popular methods has been to include a wax in the compound that will have a limited solubility, or compatibility, with the vulcanized elastomer. The wax will migrate, or bloom, on the surface of the vulcanizate and form a film of a saturated nature that is not subject to attack by ozone. This is an exacellent method for protecting a vulcanizate, provided that the wax film is continuous and flexible and is not damaged during service. Unfortunately the latter is a difficult condition to meet and any breaks in the wax film lead to very large deep cracks that may destroy the serviceability of the rubber article. An antioxidant might be expected to decompose the ozone at the surface of the vulcanizate and since it is distributed throughout the bulk of the compound, could migrate to the surface and replace antioxidant that had been consumed

in a reaction with ozone. At the optimum, then, an antioxidant would effectively compete with the elastomer in providing sites for ozone attack.

It was found that Butyl rubber requires higher loadings of wax than other polymers in order to ensure a continuous protective bloom, an observation that may be explained partly by the relatively high solubility of waxes in Butyl, and partly by the low diffusion rate of most materials through this type of polymer. Where wax is employed, a loading of more than 3 parts per hundred parts rubber is desirable. The use of antioxidants in conjunction with waxes proved beneficial; the antioxidant appeared to reinforce the protective action of the wax film, as well as retard the growth of any cracks that formed.

TABLE 7

EFFECT OF VARIOUS ANTIOXIDANTS

Base Recipe as in Table 4.

Antioxidants compared at a loading of 1 part per hundred parts rubber.

Antioxidants

1. None
2. 25 per cent di-*p*-methoxydiphenylamine, 25 per cent diphenyl-*p*-phenylene diamine, 50 per cent phenyl-beta-naphthylamine
3. Phenyl-alpha-naphthylamine
4. Acetone diphenylamine high-temperature reaction product
5. Acetone diphenylamine low-temperature reaction product
6. Acetone *p*-aminodiphenyl reaction product
7. Heptylated diphenylamine
8. Diphenyl-*p*-phenylene diamine, phenyl-beta-naphthylamine mixture
9. 65 per cent diarylamine ketone reaction product, 35 per cent diphenyl-*p*-phenylenediamine

		Outdoor exposure		
Antioxidant	Ozonizer test Rating index	Test started	First crack (days)	Rating (120 days)
1	15.0	May 12, 1953	40	5.8
2	7.7	May 12, 1953	40	3.8
3	12.0	May 12, 1953	40	4.8
4	9.5	May 12, 1953	40	2.8
5	12.5	May 12, 1953	40	3.9
6	8.0	May 12, 1953	40	4.5
7	12.0	May 12, 1953	40	4.9
8	11.4	May 12, 1953	40	4.4
9	11.8	May 12, 1953	40	4.8

As has been noted frequently in the literature, the use of wax as a protective material gives widely variable results, probably due to accidental flaws or damage to the film. In this study, the use of wax has been avoided, since it obscures the effects of other variables and gives highly variable results. A number of antioxidants were compared in a wax-free Polysar Butyl 301 recipe and the data are shown in Table 7. All the vulcanizates containing an antioxidant had a lower rating index than the control vulcanizate. The mixture of di-*p*-methoxydiphenylamine, diphenyl-*p*-phenylenediamine and phenyl-beta-naphthylamine, and the acetone *p*-aminobiphenyl reaction product gave the best protection of the antioxidants tested. In other tests, it was found that the protective action of the antioxidants increased with their concentration.

The state of cure of the vulcanizate was shown to have a large effect on the resistance to ozone in Butyl polymers. The dispersion and type of accelerator and sulfur might be expected to influence the state of cure of the vulcanizate

and the uniformity of the distribution of applied strains. The effect of these variables is shown in Table 8. A comparison of an insoluble form of sulfur and soluble sulfur is shown in Recipes 1 and 2, respectively. The compound containing soluble sulfur gave a slightly lower rating index than that with insoluble sulfur. Recipes 2 and 3 show the effect of equal molar quantities of selenium dimethyldithiocarbamate and selenium diethyldithiocarbamate. It was found that the ethyl compound gave superior resistance to ozone cracking. A similar comparison of tetramethylthiuram disulfide and tetraethylthiuram disulfide is given in Recipes 3 and 4. In this case, there was no significant difference in the rating index. Regarding the selenium accelerators, the ethyl compound has a lower melting point than the methyl compound (151° to 190° F vs. 291° to 333° F). For this reason, it might be expected that the ethyl compound would be more uniformly dispersed throughout the mix and, therefore,

TABLE 8

EFFECT OF ACCELERATOR COMBINATIONS

Base recipe:								
Polysar Butyl 301	100							
FEF black	63							
Mineral oil plasticizer	25							
Zinc oxide	4							
Magnesia (light calcined)	4							
Stearic acid	1.5							
Petrolatum	3							
Mercaptobenzothiazole	0.5							
Recipe:	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
(*a*) Tetramethylthiuram disulfide	1.5	1.5	1.5	—	1.5	1.5	1.5	—
(*b*) Tetraethylthiuram disulfide	—	—	—	1.84	—	—	—	1.84
(*c*) Selenium dimethyldithiocarbamate	2	2	—	—	2	2	2	—
(*d*) Selenium diethyldithiocarbamate	—	—	2.4	2.4	—	—	—	2.4
(*e*) Insoluble sulfur	3	—	—	—	—	—	—	—
(*f*) Soluble sulfur	—	3	3	3	3	3	3	3
Hot milling (2 min. at 307° F)	—	—	—	—	base recipe	base recipe plus (*a*)	base recipe plus (*a*) and (*c*)	base recipe plus (*b*) and (*d*)
Cure at 292° F (min.)	25	25	25	25	25	25	25	25
Modulus at 300% (lb. per sq. in.)	650	675	605	535	650	580	565	580
Ozonizer test								
Rating index	13.3	10.6	7.0	8.2	17.3	17.9	18.5	13.9
Outdoor exposure (test started May 12, 1953)								
(1) First crack (days)	50	50	50	40	40	50	50	50
(2) Rating (120 days)	3.0	3.3	2.6	2.6	5.1	4.7	4.8	1.8

that there would be less chance of having points of a low state of cure in the surface of the vulcanizate that would be more subject to attack by ozone. If the compounds were given hot milling treatments, a more similar degree of dispersion of the accelerators might be produced. The effects are shown in Recipes 5 to 8, inclusive. The hot milling for 2 minutes at 307° F with various combinations of sulfur and accelerators present resulted in a deterioration of the ozone resistance in every case. The compound containing selenium diethyl dithiocarbamate again showed the lowest rating index in this series. A consistant improvement has been found in all cases where the ethyl compound was used in the recipe.

Continuing the study of the effect of state of cure, a number of different systems of vulcanizing agents were examined. The data (Table 9) showed significant differences in ozone resistance and, indeed, the rating index varied inversely with the modulus at 300 per cent of the vulcanizate. These data give

further emphasis to the importance of obtaining a high state of cure for the best ozone resistance. The scorchy, fast-curing, *p*-quinonedioxime type systems gave the lowest rating index, with the selenium diethyldithiocarbamate compound the next best, and significantly better than the slow curing recipes that contained the *p*-tert-amylphenol derivative. These effects, however, are not considered to represent differences in the vulcanization systems as such, but rather in the states of cure of the vulcanizates.

It has been reported that a superior resistance to ozone may be obtained by varying the order of addition of carbon black and plastizicer during the com-

TABLE 9

EFFECT OF VARIOUS VULCANIZATION SYSTEMS

Base recipe:		
Polysar Butyl 301	100	
FEF black	63	
Mineral oil plasticizer	25	
Zinc oxide	4	
Magnesia (light calcined)	4	
Stearic acid	1.5	
Petrolatum	3	
Mercaptobenzothiazole	0.5	

Selenium diethyldithiocarbamate	1	—	—	—	—
Tetramethylthiuram disulfide	0.75	—	—	—	—
Sulfur	1.5	—	—	—	—
p-Quinonedioxime	—	2	—	—	—
Lead peroxide	—	4	—	—	—
p,p'-dibenzoylquinonedioxime	—	—	6	—	—
Red lead	—	—	10	—	—
Benzothiazolyl disulfide	—	—	—	0.5	0.5
Tellurium diethyldithiocarbamate	—	—	—	1	—
p-tert-amylphenol derivative	—	—	—	7	7
Zinc dibutyldithiocarbamate	—	—	—	—	0.75
Cure at 292° F (min.)	25	35	20	70	100
Hardness (Shore type A-2)	41	39	48	42	39
Modulus at 300% (lb. per sq. in.)	605	1210	940	370	340
Tensile strength (lb. per sq. in.)	1570	1360	1225	1435	1435
Elongation at break (%)	650	360	465	800	810
Ozonizer test					
Rating index	7.0	4.2	4.5	22.1	19.2
Outdoor exposure (test started July 28, 1953)					
(1) First crack (days)	32	—	58	32	32
(2) Rating (140 days)	2.2	0	<1	11.2	10.1

pounding operation[6]. This effect might be ascribed to a more uniform dispersion of these ingredients in the compound. The effects of "oil-first," "black-first," and alternate black and oil additions were examined for compounds prepared in a laboratory Type B Banbury mixer. The dispersion of carbon black in the compound was measured by the light-transmission method described by Dannenburg[7]. The oil-first procedure gave a slightly poorer dispersion of carbon black and a slightly higher rating index. The alternate addition of oil and carbon black gave a slightly lower rating index. In a similar series that contained 4 parts per hundred parts rubber of a protective wax, there was no significant difference in the ozone resistance of the vulcanizates. In addition to the fact that we have been unable to show any great improvement in ozone

resistance due to the order of addition of these ingredients, it may be significant that factory compounds showed just as good resistance to ozone as those prepared in the laboratory.

A method of improving the dispersion of carbon black in Butyl compounds has been reported by Gessler[8], that consists of heating the carbon black-Butyl mix at a high temperature, usually in the neighborhood of 400° F. The effect of milling the carbon black-Butyl masterbatch for 10 minutes in the Type B Banbury mixer at a temperature of 390° to 400° F is shown in Table 10. This

TABLE 10

EFFECT OF HOT MASTERBATCHING

Compound recipes:	A	B	
Polysar Butyl 301	100	100	Banbury Masterbatch
EPC black	63	63	
p-Dinitrosobenzene polymer, 25% mixture with 75% inert filler	—	0.5	
Mineral oil plasticizer	25	25	Cold mill
Zinc oxide	4	4	
Magnesia (light calcined)	4	4	
Stearic acid	1.5	1.5	
Petrolatum	3	3	
Mercaptobenzothiazole	0.5	0.5	
Tetramethylthiuram disulfide	0.75	0.75	
Selenium dimethyldithiocarbamate	1	1	
Sulfur	1.5	1.5	
Cure at 292° F, 25 minutes			

Recipe Banbury masterbatch treatment	A 10 min. at 210–220° F	A 10 min. at 390–400° F	B 10 min. at 390–400° F
Hardness (Shore type A-2)	41	34	35
Modulus at 300% (lb. per sq. in.)	425	885	1005
Tensile strength (lb. per sq. in.)	2190	2210	2165
Elongation at break (%)	780	570	530
Ozonizer test			
Rating index	11.0	10.4	12.7
Outdoor exposure (test started September 25, 1953)			
(1) First crack (days)	35	—	—
(2) Rating (175 days)	<1	0	0

hot-mixing treatment, with or withlut the *p*-dinitrosobenzene additive, increased the modulus of the vulcanizate, but did not significantly change the ozone resistance.

OUTDOOR TESTS

In all these tests, the vulcanizates were exposed both in the ozonizer and outdoors. The results of the outdoor exposures have been included in each of the preceding tables.

The atmospheric conditions encountered in outdoor exposure tests are widely variable, and the effects of ozone concentration, atmospheric pollution, etc , may give variable results for specimens exposed in different locations or during different seasons of the year. In the present tests, it was found that specimens exposed initially at different times during the year showed large differences in the rate of crack formation and growth. In Figure 11, the speci-

mens exposed during the winter months showed little cracking until June, when the formation of cracks was greatly accelerated, as shown by the increase in the rating value. Similar specimens exposed in the summer months of 1953 showed a rapid formation of cracks, but the growth largely stopped during the winter months. These effects indicate the necessity for comparing only specimens that were exposed outdoors during the same period of the year. If this precaution is observed, the outdoor tests show a fair correlation with tests conducted in the ozonizer. The specimens exposed outdoors, however, do not crack as fast as those tested in the ozonizer, and the cracks are likely to be fewer in number. These effects may be ascribed to the lower average ozone concentration and ambient temperature in the outdoor tests. Further, specimens exposed outdoors during the winter months may undergo considerable stress relaxation before they encounter the more severe conditions that are prevalent during the summer months.

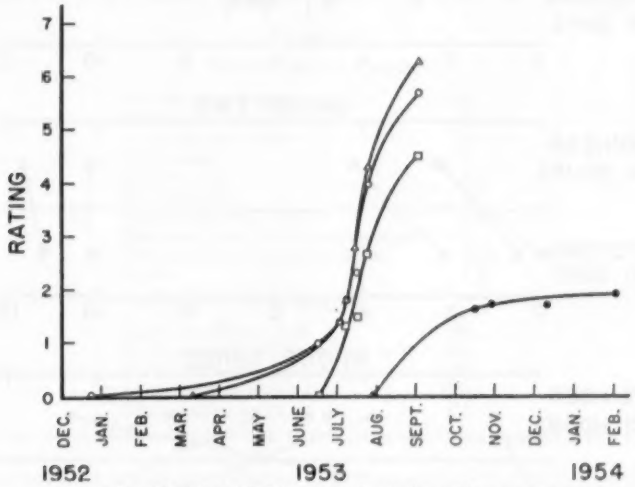


FIG. 11.—Cracking of Butyl vulcanizates during outdoor exposure.

The Polysar Butyl 400 control compound showed very little cracking during the outdoor exposure tests, and could not be used to calculate a rating index for the specimens exposed outdoors. The values shown in Figure 12 are, therefore, rating values rather than rating indexes. The relative order of values for the compounds in each test shows the degree of correlation between the two conditions, and the lines in Figure 12 connect the values for the same compound in the two tests.

Group One shows data on a series of compound with similar recipes, but with variations of the time, temperature, rotor speed of the Banbury mixing operation, and order of addition of ingredients. The compound at the left, containing selenium diethyldithiocarbamate, was significantly superior to the others, both in the ozonizer and outdoor tests. The mean rating of the other compounds, all of which contained selenium dimethyldithiocarbamate, is indicated by the center vertical line, while the lines at either side indicate the range of plus and minus twice the standard deviation of the measurement of the rating

value. There was no significant change of rating due to variations in the mixing procedure.

In Group Two are shown data for the vulcanization systems given in Table 9. Here, there was an excellent agreement between the ozonizer and outdoor tests.

Group Three shows data for various plasticizers, and here there are instances of both good and poor agreement between ozonizer and outdoor performance.

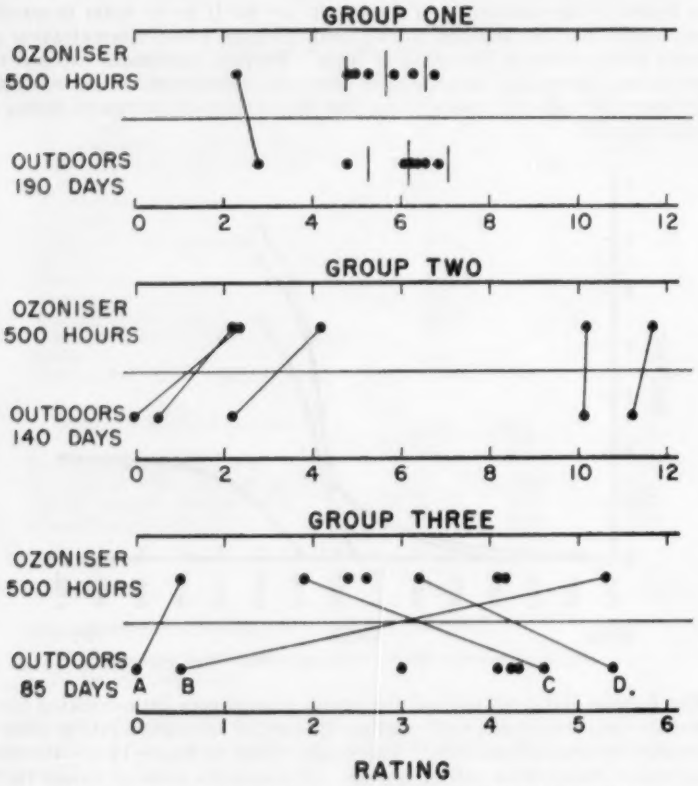


FIG. 12.—Comparisons of ozonizer and outdoor cracking of Butyl compounds.

The coal-tar plasticizer (A) showed excellent resistance in both tests, no cracks developing during the outdoor exposure. On the other hand, the cumarone-indene resin (B) gave severe cracking in the ozonizer, but showed a rating of less than one after the outdoor exposure. In this instance, stress relaxation may well account for the disagreement. Compounds (C) and (D), containing, respectively, a mineral-oil plasticizer and an ester plasticizer, showed relatively better resistance in the ozonizer than outdoors.

The findings in this examination of the ozone cracking of Polysar Butyl compounds may be summarized by the optimum weatherstrip recipe given in

Table 11. The Polysar Butyl 301 elastomer has the desired low degree of unsaturation to provide superior resistance to ozone cracking. Since it is a high molecular-weight elastomer, it can be compounded with relatively high proportions of plasticizer and carbon black to provide good processibility without deteriorating the physical properties of the vulcanizate.

A selected coal-tar distillate has been employed as the plasticizer, since it was found to give very good ozone resistance. Similarly, selenium diethyldithiocarbamate was used because of its proven superiority to the methyl compound.

The cure of 30 minutes at 307° F provides a high state of cure in this recipe, and this is a most important factor in obtaining good resistance to ozone.

The physical properties of this compound meet the requirements of an R 515 compound (ASTM classification), and the ozone rating index was less than 1.

While no antioxidant was included in this recipe, an improvement of ozone resistance would be obtained by the addition of one of the more effective agents.

TABLE 11

WEATHERSTRIP RECIPE

Polysar Butyl 301	100
FEF black	63
Coal-tar plasticizer*	25
Zinc oxide	4
Stearic acid	1.5
Petrolatum	3
Mercaptobenzothiazole	0.5
Selenium diethyldithiocarbamate	1
Tetramethylthiuram disulfide	0.75
Sulfur	1.5
Cure at 307° F, 30 minutes	
Hardness (Shore A-2)	48
Modulus at 300% (lb. per sq. in.)	550
Tensile strength (lb. per sq. in.)	1660
Elongation at break (%)	630
Ozone rating index	<1

* An amber-colored refined coal-tar distillate, Sp. Gr. 1.00 to 1.04, boiling range 230 to 310° C.

Wax was not used in this compound so as to demonstrate that Butyl compounds could be developed with good ozone resistance without resorting to the use of wax.

It was not possible to show in the laboratory that the order of oil and black addition had a significant effect on the ozone resistance of the vulcanizate. However, the data indicated that a rapid method of mixing the elastomer with oil and carbon black gave some improvement in the resistance to ozone. In the factory operations, alternate addition of oil and carbon black might be the best means of obtaining a processable compound in a minimum time.

SUMMARY

A study of the cracking behavior of Butyl-rubber vulcanizates, exposed under static strain in an atmosphere containing 25 parts of ozone per 100 million parts by volume of air, is described. An account is given of sampling and testing procedures, including the development of a means of rating the severity of cracking in triangular strip specimens. The factors studied include polymer unsaturation, black and oil loadings, antioxidants, state of cure, and mixing

variations. Cracking increases moderately with increasing raw polymer unsaturation, and is markedly reduced with increasing state of cure. Black loadings in excess of 40 parts per 100 parts of polymer are desirable. Plasticizers are generally detrimental to ozone resistance; the effect is proportaional to plasticizer loading, but varies considerably between plasticizers. The antioxidants tested were all of some benefit, but none offered complete protection at conventional loadings. Variations of laboratory mixing and processing techniques caused no substantial change in cracking behavior. By the careful choice of compounding ingredients and the use of a high state of cure, it is possible to prepare low-cost, highly resistant compounds without reliance on waxes or excessive antioxidant loadings.

ACKNOWLEDGMENT

The authors wish to express their thanks to Polymer Corporation Limited for permission to publish this paper.

REFERENCES

[1] Crabtree and Kemp, *Ind. Eng. Chem. Anal. Ed.* **18**, 769 (1946).
[2] Foulk and Bowden, *J. Am. Chem. Soc.* **48**, 2045 (1926).
[3] ASTM Test Designation D 1171-51T.
[4] Reconstruction Finance Corporation, Office of Rubber Reserve, "Specifications for Government Synthetic Rubbers", Washington, D. C.
[5] Crabtree and Kemp, *Ind. Eng. Chem.* **38**, 237 (1946); Cuthbertson and Dunnom, *Ind. Eng. Chem.* **44**, 834 (1952).
[6] Jackson, E. D., paper presented at the 35th Annual Conference, Chemical Institute of Canada, June 1952.
[7] Dannenberg, *Ind. Eng. Chem.* **44**, 813 (1952).
[8] Gessler, *Rubber Age* (N. Y.) **74**, 59 (1953).

OZONE CRAZING OF BIAXIALLY STRESSED GR-S VULCANIZATES *

Z. T. Ossefort and W. J. Touhey

Ordnance Corps., U. S. Army, Rock Island Arsenal, Rock Island, Illinois

It is a generally recognized phenomenon that the surface of stressed GR-S vulcanizates is subject to cracking on aging[1] (unless protected by the presence of suitable antioxidants). This cracking has for many years been considered to be of two distinct types:

1. Regular cracking formed perpendicular to the axis of stress and caused by ozone in the atmosphere.
2. Irregular cracking or crazing, which is usually not so deep and follows no pattern with respect to the axis of stress. This has been attributed to light activated oxidation[2].

Since even the regular cracking was for a great many years attributed to the action of light and was erroneously referred to as sun checking, the possibility was entertained that both types may be manifestations of ozone attack and that the differentiating feature between the two is the manner under which the rubber is stressed.

Table 1

Compound Formulation

GR-S 1505	100
Philblack A*	50
Zinc oxide	3
Stearic acid	2
Neozone D†	1
Agerite Resin D‡	1
Santocure§	1
Sulfur	1.75
Cure: 30 minutes @ 307° F	

* Phillips Chemical Co., Akron, O.
† E. I. du Pont de Nemours & Co., Wilmington, Del.
‡ R. T. Vanderbilt Co. New York, N. Y.
§ Monsanto Chemical Co., Akron, O.

It was, therefore, the purpose of this work to determine whether typical crazing of stressed GR-S vulcanizates could be produced by ozone in darkness.

EXPERIMENTAL PROCEDURE

Cross-shaped specimens 3- by 3- by 0.080 inch were cut from vulcanized pads. These pads were prepared from a typical tread-type GR-S stock, the formula of which is given in Table 1.

These specimens were subjected to varying amounts of biaxial stress, and the areas of greatest stress protected by covering with tape to prevent greater

* Reprinted from the *Rubber World*, Vol. 132, No. 1, pages 62–63 and 70, April 1955.

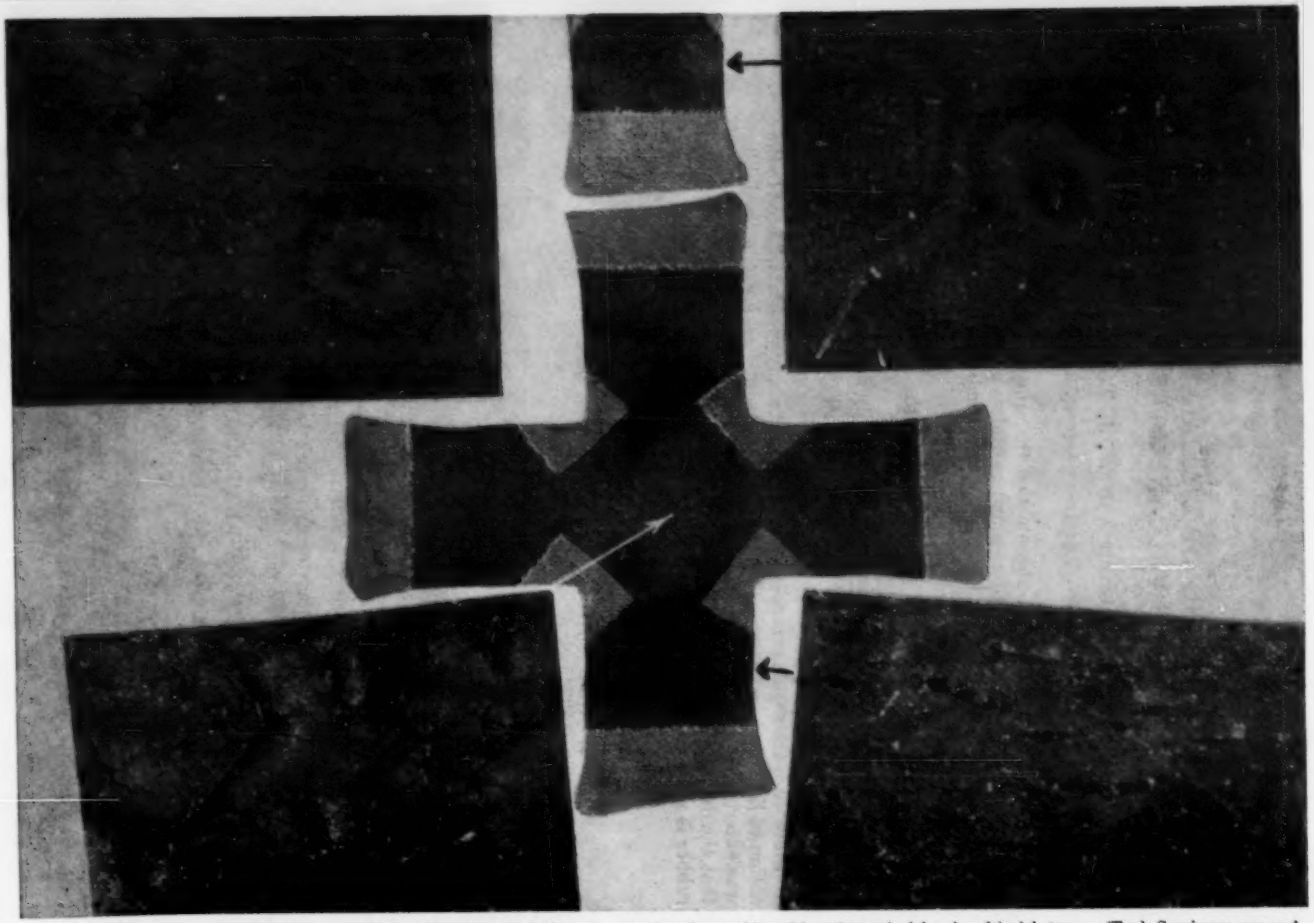
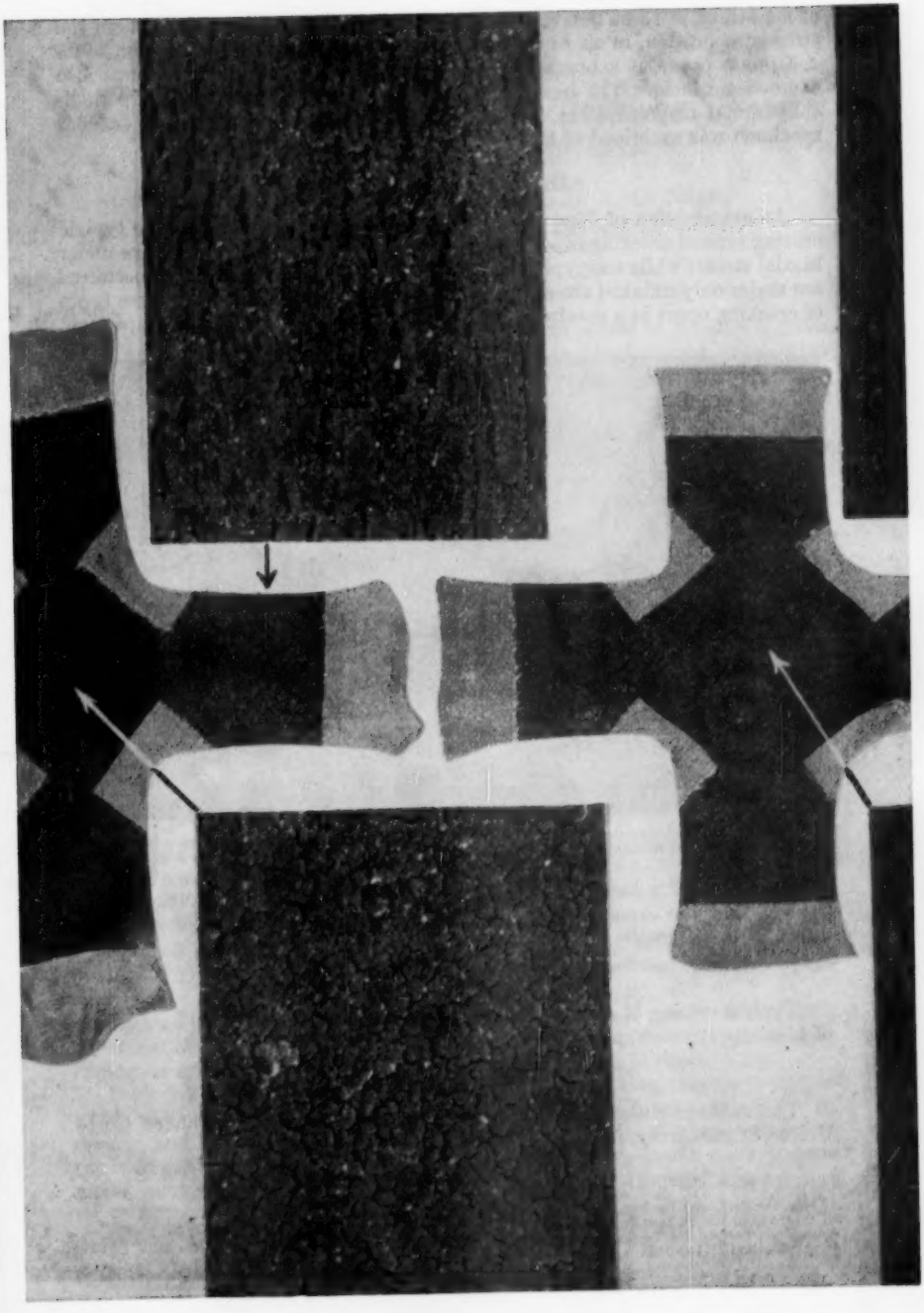


FIG. 1.—GR-S tread stock specimens exposed in ozone cabinet in dark, and exposed outdoors while subjected to uniaxial and multiaxial stress. (Top) Specimens exposed 43 hours in ozone cabinet; sample on right was stressed 12½% in one direction; while sample on left was stressed 12½% in two directions. Examined under a magnification of 20 times. (Middle) Specimens exposed 24 hours in ozone cabinet; sample on right was stressed 16% in one direction; while sample on left was stressed 9% in one direction and 16% in the other. Magnification 20 times, as above. (Bottom) Specimens exposed four days outdoors. Sample on right had 12½% stress in one direction; sample on left had stress of 12½% in two directions. Magnification 20 times.



20 times. (Middle) Specimens exposed 24 hours in ozone cabinet; sample on right was stressed 16% in one direction; white sample on left 16% in the other. Magnification 20 times, as above. (Bottom) Specimens exposed four days outdoors. Sample on right had 12½% stress in one direction; sample on left had stress of 12½% in two directions. Magnification 20 times.

ozone attack at these points. The specimens were then exposed, while in the stressed condition, in an ozone cabinet[3] in darkness, at a concentration of 25 ±5 pphm ozone at a temperature of 100°(±2°) F. One specimen was also exposed outdoors. The specimens in the ozone cabinet were examined periodically at 20 magnifications for visual evidence of cracking, and the outdoor specimen was examined at five magnifications.

RESULTS AND DISCUSSION

An examination of Figure 1 (*top and middle*) will indicate that the typialc crazing type of cracking is present in the areas of the specimen which are under biaxial stress; while the typical ozone cracking is present where the specimens are under only uniaxial stress. As shown in Figure 1 (*bottom*), the same types of cracking occur in a specimen exposed four days outdoors. For comparison,

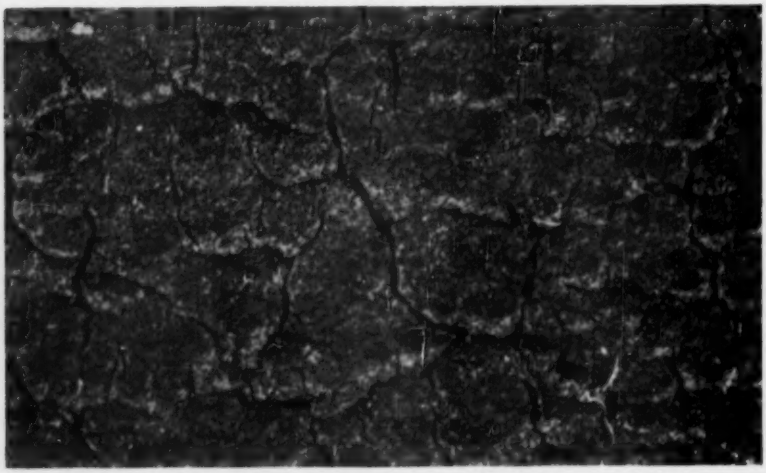


FIG. 2.—Typical crazing of tire sidewall after several thousand miles of service. Similarity between this crazing and that induced by ozone exposure of biaxially stressed stocks of Figure 1 is evident.

a photograph of a badly crazed tire sidewall is furnished in Figure 2. It is evident that the experimentally produced crazing is identical with that produced in tire sidewalls during service.

CONCLUSION

Typical crazing of stressed GR-S vulcanizates can be produced by exposure of biaxially stressed specimens to ozone in the absence of light.

ACKNOWLEDGMENT

The authors wish to express their appreciation to the Ordnance Corps, United States Army, for permission to publish this paper.

REFERENCES

[1] Shaw, Ossefort, and Toubey, *Rubber World* **130**, 636 (1954).
[2] Crabtree and Kemp, *Ind. Eng. Chem.* **38**, 2781 (1946); Winkelmann, *Ind. Eng. Chem.* **44**, 841 (1952).
[3] American Society for Testing Materials, "ASTM Methods for Rubber Products", Dec. 1952", ASTM Method D1149-51T.

SOFTENING OF VULCANIZED CARBON BLACK-LOADED RUBBER DURING EXTENSION *

D. G. MARSHALL, D. L. WALKER, AND J. G. SMITH

PHYSICAL RESEARCH DIVISION, DUNLOP RUBBER CO., LTD.,
FORT DUNLOP, BIRMINGHAM, ENGLAND

INTRODUCTION

A sample of vulcanized rubber requires a greater stress to produce a given extension during its first elongation than that required during subsequent elongations. This behavior has been well known of rubber for many years and was reviewed in a text-book as early as 1920[1]. Early investigators regarded this phenomenon as an obstacle in the way of reproducible data, although more recently[2] the softening process has itself been studied as a source of useful information.

Two theories have been advanced to explain the details of this softening effect. In one advanced by Blanchard and Parkinson[3], the softening is described in terms of an extension of James and Guth's theory. In another, that of Mullins and Tobin[4], rubber is considered as a heterogeneous system consisting of a hard phase and a soft phase. The hard material is regarded as being softened by stress and the amount of hard material as being determined by the maximum previously applied stress.

A difference between the stress-extension characteristics during the first cycle from those obtained during subsequent cycles is to be expected from the fact that rubber is a viscoelastic material, and not simply an elastic material. The object of the present paper is to compare the stress-extension properties of rubber with those to be anticipated from a simple viscoelastic material.

STRESS–EXTENSION BEHAVIOR OF VISCOELASTIC MODELS

A viscoelastic material is often represented as a distribution of Maxwell elements possessing a spectrum of relaxation times[5].

In order to appreciate qualitatively how such a system will behave, the simple model shown in Figure 1 (*a*) may be considered.

Figure 2 represents two successive cycles of extension and retraction of the model. Figure 3 represents two similar cycles for a black-loaded rubber specimen.

Figure 4 represents a series of successive extensions of the model. Figure 5 is taken from a paper by Mullins and Tobin[4] and illustrates the results of an analogous experiment performed on a black-loaded natural rubber sample.

Figures 2 and 4 were derived from the electrical analog (Figure 1 (*b*)), in which the charges on the condenser are equivalent to the extensions of the springs, and the potentials across the condensers are equivalent to the forces on the springs. The choice of relaxation times is arbitrary, since a more realistic model would involve a distribution of relaxation times. Figures 2 and 4 were

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 31, No. 4, pages 115–125, August 1955.

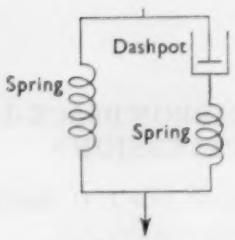


FIG. 1(a).

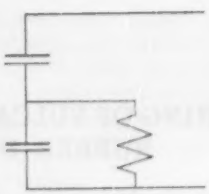


FIG. 1(b).

obtained with relaxation times of the same order as the times taken to extend the model.

There are two main differences between the softening effects exhibited by the simple model and those shown by black-loaded rubber. First, the model exhibits much greater permanent set than actual rubber. Second, the softening and permanent set are more permanent for rubber than for the model which would not remain substantially softened for much longer than the time of the experiment.

THERMODYNAMIC EXPERIMENTS

In order to understand the softening effect, it is important to ascertain whether the mechanical energy dissipated in softening a rubber sample during the initial elongation appears as an internal energy change or whether it appears as heat. An absolute determination of the heat changes accompanying successive deformations would be a formidable undertaking, so that an attempt has been made to investigate energy changes by means of measurements of relative temperature rises.

THEORY OF METHOD

Figure 3 shows typical load-extension curves taken during two successive cycles of extension and retraction (OPAQO and ORBSO, respectively) of a

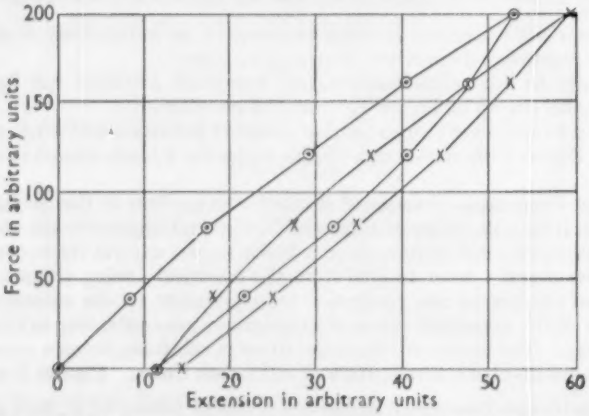


FIG. 2.—The first two cycles of extension and retraction of a viscoelastic model.

sample of carbon black-loaded rubber. As the sample is stretched, its temperature rises. Let us suppose that we are dealing with adiabatic conditions and that the temperatures θ_1, θ_2, θ_3, θ_4 and θ_5 are temperatures initially, after the first extension, after the first retraction, after the second extension, and after the second retraction, respectively. The area under the curve OPA represents

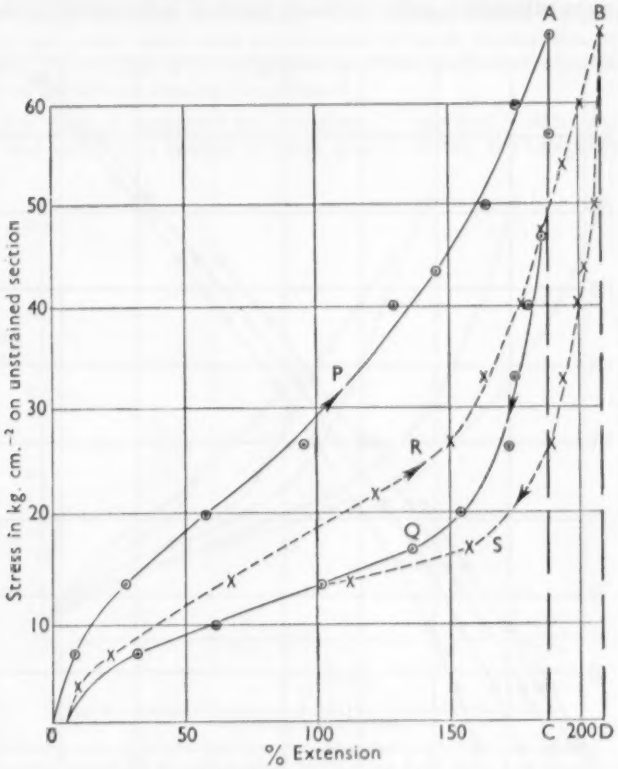


FIG. 3.—The first two-extension cycles of vulcanized natural rubber loaded with 40 parts of HAF black.

the work done in stretching the sample to A, and is made up of the following energy changes:

(1) The energy required to overcome the rubber elastic forces.
(2) The energy required to overcome the rubber viscous forces.
(3) The work done in softening the rubber.

The energies involved in processes (1) and (2) appear as heat, in both cases ignoring the slight changes in internal energy that occur on stretching rubber. The energy involved in process (3) will not appear entirely as heat if the softening process involves any potential energy change or heat of reaction.

When the rubber is released, the energy involved in process (1) is absorbed and the temperature drops. The area under the curve is equal to the work done by the sample. This energy is accounted for by the difference between the temperature drop due to a reversal of process (1) and the temperature rise due to process (2). In the case of retraction, there is no reason to suppose process (3) to be taking place. During the second cycle, the process (3) may be ignored, since subsequent cycles are nearly identical to the second cycle.

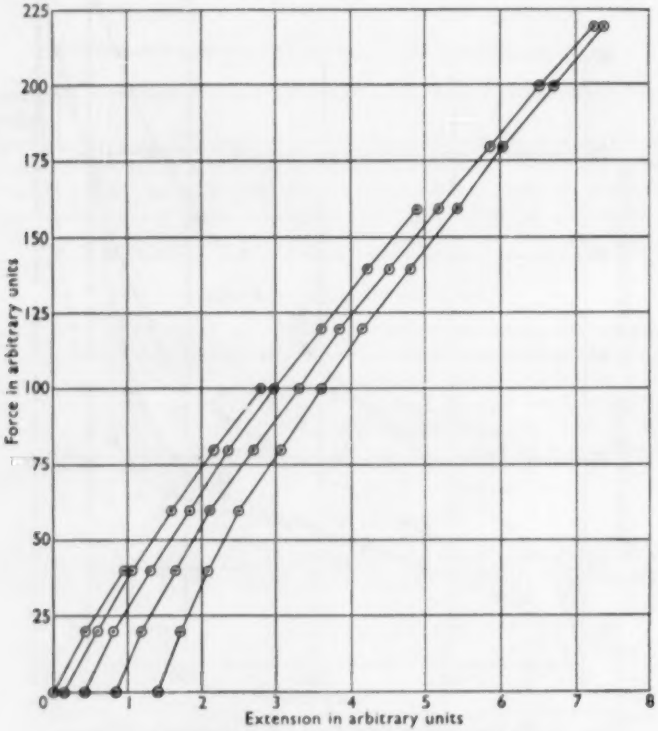


FIG. 4.—Successive extensions of a viscoelastic model.

From the foregoing discussion, it follows that the following equations should be true:

$$\frac{\text{Area enclosed by ORBSO}}{\text{Area enclosed by OPAQO}} = \frac{\theta_5 - \theta_3}{\theta_2 - \theta_1 + C} \tag{1}$$

$$\frac{\text{Area enclosed by ORBSO}}{\text{Area enclosed by OPACO}} = \frac{\theta_4 - \theta_3}{\theta_2 - \theta_1 + C} \tag{2}$$

where C is proportional to the energy used up by process (3). The quantity C can, therefore, be found from successive load-extension curves and the tempera-

ture changes accompanying extension and retraction. There will obviously be a number of other ratios involving these quantities, but Equations (1) and (2) were found convenient to investigate experimentally.

EXPERIMENTAL METHODS

The adiabatic experiment discussed above cannot be performed easily because of cooling during the experiment. The response time of the temperature recording equipment sets a limit to the speed at which the experiment may be performed. Two types of investigation have been performed which are modifications of the simple idealized experiment.

(1) The method suggested by Equation (1) was used. After rapidly extending and releasing a sample of black loaded rubber, the temperature of a

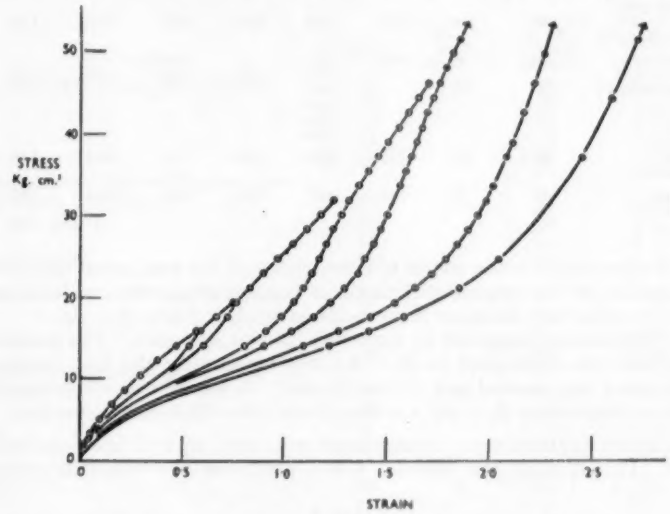


FIG. 5.—Successive extensions of vulcanized natural rubber loaded with 50 parts MPC black.

thermocouple attached to the rubber surface at first rises and finally drops as the sample cools. The maximum temperature reached after the extension and retraction was recorded and regarded as equivalent to $(\theta_2 - \theta_1)$. After the sample had cooled to its initial temperature, it was again rapidly stretched, released, and a second temperature rise equivalent to $(\theta_3 - \theta_2)$ was measured.

Temperature changes were recorded with thermocouples and a galvanometer. Five copper-constantan thermocouples (38 S.W.G. wires) were connected in series and were stuck to the surface of each rubber sample with an adhesive rubber solution. Dumbbell-shaped specimens having a straight section $3 \times 1 \times 6$ mm. were used in these experiments.

Load-extension curves, from which the area OPAQO and ORBSO were determined, were measured with separate samples, using an apparatus in which the extension was performed manually, and the load measured with a spring balance. The difference in rate of extension between the thermal and me-

TABLE 1

Black	Parts per hundred rubber	Max. stress (kg. cm^{-2})	Max. % extension during 1st cycle	Thermal ratios	Mean thermal ratio	Mechanical ratios	Mean mechanical ratios	Mean thermal ratio / Mean mechanical ratio
*Electrically conductive channel black (Spheron-C)	70	73	110	0.46 0.45	0.46	0.41 0.44	0.43	1.07
*Electrically conductive channel black (Spheron-C)	70	105	134	0.43 0.51 0.43 0.45 0.51	0.47	0.38 0.39	0.39	1.20
Electrically conductive channel black (Spheron-C)	70	50	47	0.68	0.68	0.70	0.70	0.97
Electrically conductive channel black (Spheron-C)	40	100	240	0.60	0.60	0.53	0.53	1.13
Electrically conductive channel black (Spheron-C)	40	67	200	0.72 0.71 0.41 0.44 0.50 0.63	0.57	0.58 0.54	0.56	1.02
HAF Black (Philblack-O)	62.5	100	112	0.55	0.55	0.51 0.52	0.52	1.06
HAF Black (Philblack-O)	40	67	184	0.50	0.50	0.54	0.54	0.93
							Average	1.05

chanical experiments was a source of error, although the area ratios were found not to depend on the rates or techniques of measurement over a wide range of speeds, provided that the same procedure was employed in each cycle.

(2) The method suggested by Equation (2) was also used. The maximum temperature rise equivalent to $(\theta_2 - \theta_1)$ was found after the first extension. The specimen was released and allowed to cool. A second maximum temperature rise equivalent to $(\theta_4 - \theta_3)$ was then found after the second extension.

The same thermocouple arrangement was used as had been applied to method (1), although the thermal e.m.f. produced was recorded with an

TABLE 2

Black	Parts per hundred rubber	Max. stress (kg. cm^{-2})	Max. % extension during 1st cycle	Thermal ratios	Mean thermal ratio	Mechanical ratios	Mean mechanical ratios	Mean thermal ratio / Mean mechanical ratio
*Electrically conductive channel black (Spheron-C)	70	73	110	0.63 0.55	0.59	0.61 0.60	0.61	0.97
HAF Black (Philblack-O)	70	67	75	0.82 0.70	0.76	0.82 0.86	0.84	0.09
HAF Black (Philblack-O)	62.5	100	112	0.73 0.79	0.76	0.75	0.75	1.01
HAF Black (Philblack-O)	40	67	184	0.73 0.74	0.74	0.82	0.82	0.90
Acetylene black (Shawinigan)	40	67	150	0.84 0.79	0.82	0.86	0.86	0.95
	40	67	205	0.67	0.77	0.84	0.84	0.92
Heat-treated Channel black				0.96 0.68				
							Average	0.94

amplifier and pen recorder (an Ediswan Electro physiological amplifier was modified to produce a 15 second time constant).

RESULTS

Table 1 shows the results of the experiments of type (1). The area ratios $\frac{ORBSO}{OPAQO}$ cannot be considered as significantly different from the temperature ratios $\frac{(\theta_3 - \theta_2)}{(\theta_2 - \theta_1)}$.

TABLE 3

LOAD–EXTENSION DATA ON BLACK–LOADED COMPOUNDS AT VARIOUS TEMPERATURES

Black loading	Temperature	Max. load (kg. cm.$^{-2}$)	* Load in kg. cm.$^{-2}$ at 50% extension	$\frac{ORBSO}{OPAQO}$
50 parts MPC black (Micronex)	22	32	23	0.53
	40		20	0.69
	56		19	0.53
	70		18	0.55
	90		17	0.51
50 parts electrically conductive channel black (Spheron-C)	22	31	25	0.65
	40		22	0.64
	63		21	0.58
	81		20	0.54
50 parts acetylene black (Shawinigan)	22	29	26	0.52
	40		25	0.48
	70		23	0.48
	78		20	0.56
50 parts graphitized channel black (Graphon)	22	12	4.5	0.56
	42		4.4	0.63
	61		4.0	0.59
	85		3.7	0.67
40 parts electrically conductive channel black	22	50	18	0.58
	64		15	0.51
70 parts electrically conductive channel black	22	100	51	0.41
	64		37	0.48
40 parts HAF black (Philblack-O)	22	50	17	0.59
	64		13	0.47

* The loads at 50 per cent extension were determined during the initial extension.

Table 2 shows results of the experiments of type (2). Again the area ratios cannot be considered as significantly different from the temperature ratios. From these two experiments if may, therefore, be concluded that over 90 per cent of the energy used in softening the rubber during the first extension appears as thermal energy.

In both tables of results the data refer to successive elongations taken to the same stress, except for that marked with an asterisk, in which successive elongations were taken to the same strain. It is apparent that, for each technique, the mechanical ratios are similar over a range of loadings and extensions.

The result that over 90 per cent of the energy used in softening the rubber

appears as heat places a limit on the energy available for breaking chemical bonds or for effecting a change of state in the rubber. Any theory that postulates a bond-breaking mechanism must stipulate the numbers and strengths of bonds which result in only a small proportion of the mechanical energy available being used up in breaking them.

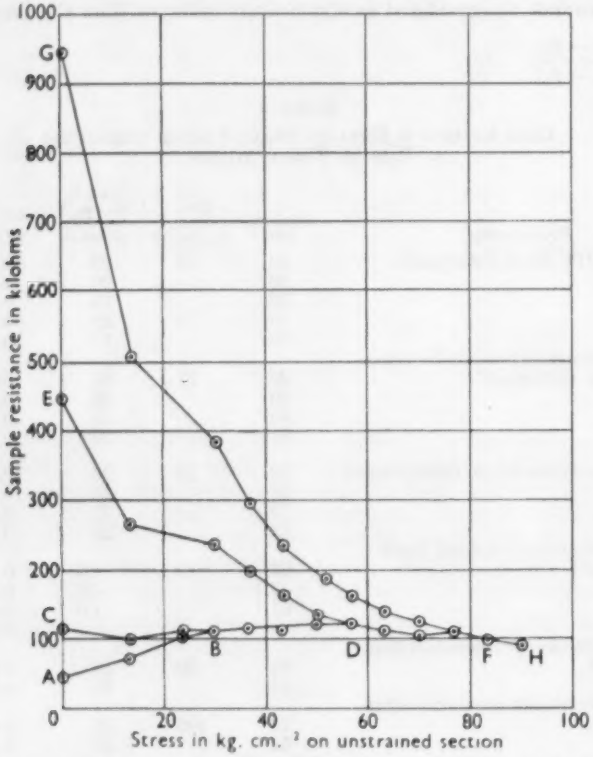


FIG. 6.—Conductivity changes accompanying successive extensions of vulcanized natural rubber loaded with 62.5 parts of HAF black.

SOFTENING AT TEMPERATURES ABOVE ROOM TEMPERATURE

Load-extension curves were obtained at temperatures ranging from 22° to 90° C. A separate sample was used at each temperature, and in each case the first two cycles of extension and retraction were observed, each cycle being taken to the same maximum stress. The load was increased incrementally at intervals of 30 seconds, and readings were taken just before each additional extension. A complete cycle of extension and retraction occupied 4 minutes.

Table 3 shows the area ratio $\frac{\text{ORBSO}}{\text{OPAQO}}$ (see Figure 3) and the modulus during the first extension. The area ratio showed no significant variation with

temperature, although the modulus varied systematically in the same temperature range.

In every case the modulus fell as the temperature rose. This result agrees with other work on the temperature variation of modulus of black-loaded rubbers[6]. A fall of modulus with rise of temperature (although not predicted by the kinetic theory of rubber elasticity for equilibrium conditions) is characteristic of a material in which the viscous contribution to the stress-extension behavior is important.

ELECTRICAL RESISTANCE CHANGES ACCOMPANYING SOFTENING

Conductivity changes occurring during the softening process should provide some indication of any changes of carbon black geometry that occur. The behavior indicated in Figure 6 for a sample containing 62.5 parts of HAF black per hundred of rubber is typical of several results obtained with high loadings of carbon black in rubber. A rubber sample was first stretched until stress B was reached; the resistance changes during extension followed the curve AB. The specimen was then released and the resistance rose. On further stretching the specimen to stress D, the resistance followed the curve CD. At stress D the sample was retracted, and during further extension to stress F the resistance followed the curve EF. This procedure was repeated up to stress H. During a subsidiary experiment, the resistance changes accompanying the direct extension of a specimen to stress H followed the curve ABDFH.

Qualitatively such results do not depend on timing procedure, although quantitatively there is time dependence resulting from the gradual return of the sample resistance to its initial value after stretching and releasing. The time scale followed in the experiment resulting in Figure 6 involved one minute elapsing after each incremental extension prior to a resistance measurement, and five minutes elapsing between the retraction and the determination of the resistance of the unstressed sample.

The behavior described above corresponds closely to the well known stress-extension behavior illustrated in Figure 5. The similarity between the effects of repeated prestressing on both the mechanical properties and the electrical resistance suggests that the softening process is accompanied by a change in the arrangement of the carbon black particles.

GENERAL TECHNIQUE

In view of the diversity of types of mechanical experiment, it was found desirable to use a simple manually operated device for determining stress-extension behavior. The loads were measured with a spring balance, and the extension was performed incrementally with a regular interval between successive extensions, so that the same procedure was employed in all curves that were compared.

The compounds used in these experiments contained:—natural rubber 100 parts by weight; sulfur 3; mercaptobenzothiazole 1; zinc oxide 5; stearic acid 3; Nonox-HFN 1; varying amounts of black specified in the text; vulcanized 50 minutes at 139° C, with 15 minutes rise time.

CONCLUSIONS AND DISCUSSION

The results of the observations recorded in this paper may be summarized by the following items.

1. A difference between the first and second load-extension curves is to be expected in any viscoelastic material, although the behavior of black-loaded rubber at large extensions differs in some fundamental respects from a simple viscoelastic material.
2. Within the experimental limits of about ±10 per cent, all of the energy used in softening the black-loaded rubbers studied appears as heat.
3. The ratio between the area of the hysteresis cycle obtained on first stretching a specimen of black-loaded rubber and that obtained during the second extension varies only slightly from compound to compound in the range of extensions studied.
4. Although the modulus of a black-loaded rubber decreases with increasing temperature, the ratio between the hysteresis area of the first extension and that of the second extension remains roughly constant over the temperature range studied.
5. There are electrical resistance changes that correspond closely to the mechanical softening effects experienced with black-loaded rubber.

Result (2) suggests that if cross-linkage breaking or changes of state of rubber are specified as mechanisms for producing softening, then the potential energy changes required must be small, compared with the mechanical energy available.

Result (5) shows that changes in arrangement of the carbon black particles are associated with the softening process, and therefore suggests that the softening is related to internal strains in the rubber.

These results do not prove that the softening observed in rubber is similar in principle to the behavior of a simple viscoelastic model during the first and other extensions. However, these observations are consistent with this view, except for the difficulty connected with the relationship between the softening and the permanent set in the simple viscoelastic material, and the difficulty connected with the persistence of softening. A simple linear model is obviously bound to have considerable limitations in describing the properties of a black-loaded rubber at high extensions. The limitations may arise from the non-linearity of rubber elasticity and the non-Newtonian nature of rubber flow; alternatively, it may be necessary to postulate some entirely different process, such as rubber heterogeneity[4] or mechanical bond breaking[5].

ACKNOWLEDGMENTS

We are indebted to E. F. Powell for suggesting that conductivity changes might accompany the softening of black-loaded rubber. We are grateful to D. Bulgin and A. F. Blanchard for many interesting discussions, and to L. Mullins and N. R. Tobin for permission to reproduce Figure 5.

In conclusion we wish to thank the Dunlop Rubber Co., Ltd., for permission to publish this paper.

REFERENCES

[1] Schidrowitz, "Rubber", Methuen, London, 1920, p. 236.
[2] Holt, *Ind. Eng. Chem.* **23**, 1471 (1931); Mullins, *J. Rubber Research* **16**, 275 (1947); Blanchard and Parkinson, *Ind. Eng. Chem.* **44**, 799 (1952).
[3] Blanchard and Parkinson, *Ind. Eng. Chem.* **44**, 799 (1952).
[4] Mullins and Tobin, paper presented at the Third Rubber Technology Conference, London, June 22–25, 1954.
[5] Alfrey, "Mechanical Behavior of High Polymers", Interscience Publishers, Inc., New York, 1948.
[6] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944); Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945); Waring, *Ind. Eng. Chem.* **43**, 352 (1951).

CORRELATION OF ROOM-TEMPERATURE SHELF AGING WITH ACCELERATED AGING *

R. A. YOUMANS AND G. C. MAASSEN

R. T. VANDERBILT CO., INC., 230 PARK AVE., NEW YORK, N. Y.

In 1931, a series of compounds was mixed to obtain data for publication purposes. After the necessary data for use at that time had been obtained, the remaining vulcanized test slabs of each compound were tied together in a bundle and stored in a desk drawer without wrapping.

The compounds used for this series of tests contained different percentages of antioxidant. After being stored for 22 years, the several stocks were analyzed to determine whether there had been any migration of antioxidant from stocks containing antioxidant to those containing no antioxidant. A definite migration was found; compounds that had originally contained no antioxidant definitely showed its presence. It was, therefore, decided in this work to use a compound that had originally contained antioxidant, so that the results would not be affected by the gradual acquisition of an antioxidant.

The selected compound had the following formulation:

Pale crepe	50
Smoked sheet	50
Zinc oxide	5
Channel black	40
Pine tar	2
Stearic acid	4
Phenyl-2-naphthylamine	2
Mercaptobenzothiazole	1
Sulfur	3

After 22 years, the antioxidant content of this compound had dropped from 2 parts to 1 part on the rubber hydrocarbon.

A similar stock originally made without antioxidant had, during the 22 years of storage, acquired enough antioxidant so that it contained 0.2 per cent, based on the rubber content. This amount of antioxidant evidently had been acquired by volatilization and migration from stocks containing the antioxidant.

At intervals during the course of the 22 years, the physical properties of these stocks were determined. The percentage change of physical characteristics of the compound is shown in Figure 1.

The tensile and elongation properties[1] depreciated at a fairly uniform rate during the entire 22-year period. The modulus showed a very rapid increase during the early stages of storage, a maximum at the end of about 12 years, and a gradual decline to 22 years. The phenomenon known as reversion in natural rubber had not yet occurred. Although the modulus showed an indication of dropping, the elongation had not yet begun to increase; it can be assumed that,

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 47, No. 7, pages 1487–1490, July 1955. This paper was presented at the meeting of the Division of Rubber Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September 12–17, 1954. The present address of R. A. Youmans is the Kirkhill Rubber Co., Brea, California.

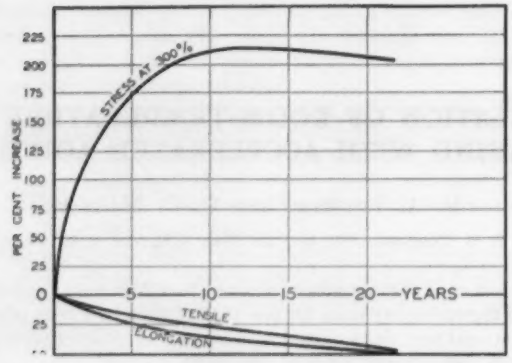


FIG. 1.—Change of physical properties with natural aging.

at the end of 22 years, this compound had not begun to revert, as reversion is ordinarily known in the rubber industry.

To try to correlate these data with accelerated aging tests, the compound was remixed and subjected to several types of accelerated aging tests—the air oven[2] at 70° C, the oxygen bomb at 70° C and 300-pound pressure[3], and the air bomb at 127° C and 80-pound air pressure[4]. To avoid the possibility of migration of antioxidants, all the accelerated aging was done in individual containers.

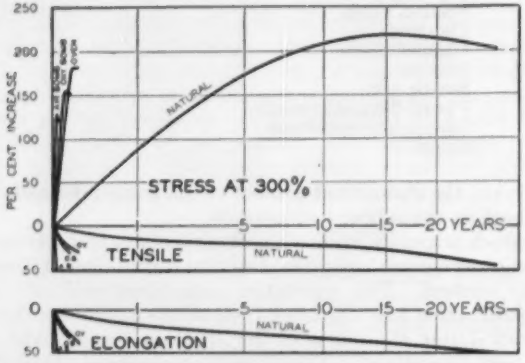


FIG. 2.—Change of physical properties with natural and accelerated aging.

The information for both natural shelf-life aging and accelerated aging is shown in Figure 2.

The curves on the left are very much cramped, and it is difficult to make any definite correlation. By selecting convenient time intervals along the horizontal axis for each set of aging conditions, it is possible to spread the curves so that correlation is possible. Figure 3 shows the curves for tensile depreciation. From these curves Table I, giving percentage tensile depreciation equivalents, was developed.

From these data it can be seen that, given a sufficient exposure in the oxygen bomb or air bomb, it is possible to cause tensile depreciation equal to that obtained on natural aging for almost any period. The air oven curve changes slope and tends to level off. Unfortunately, in their work the authors did not continue the oxygen bomb or air-oven tests long enough to get correlations to 21 years. However, it is seen that 6 days in the oxygen bomb is the equivalent of 14 years of natural aging, 21 days in the air oven is equivalent to 14 years of aging, 97 minutes in the air bomb is the equivalent of 14 years, and 173 minutes in the air bomb is the equivalent of 21 years.

Using similar time intervals on the horizontal axis, curves were drawn for elongation properties (Figure 4). From these curves a correlation can be had

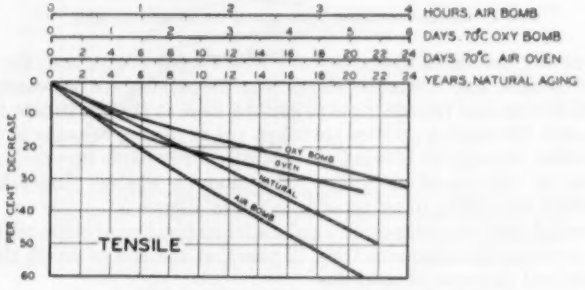


FIG. 3.—Tensile depreciation with natural and accelerated aging.

among natural, air bomb, and oven aging. However, because of the change in slope in the curve for oxygen-bomb aging, the correlation is limited.

From the curves in Figure 4, Table II, showing percentage elongation depreciation equivalents, has been developed.

From these data it is evident that the oxygen bomb can be used to predict the elongation changes by natural aging up to 10 years. At that point, the curve starts to level off to such an extent that it is difficult to obtain further correlation. The air oven deteriorates the elongation properties in 21 days to about the same extent as 22 years of natural aging, or 220 minutes in the air bomb.

The air bomb and air oven depreciation curves approximately parallel the natural aging depreciation curve for elongation. However, the oxygen bomb curve tends to become level, and correlation is limited to 10 years.

TABLE I

TENSILE EQUIVALENTS

Natural aging (years)	70° Oxygen bomb (days)	70° Air oven (days)	Air bomb (min.)
1	0.17	0.5	5
2	0.41	1.25	13
3	0.75	1.75	18
4	1.13	2.50	25
5	1.5	3.50	32
14	6.0	21.+	97
15	Test discontinued		105
18			143
21			173

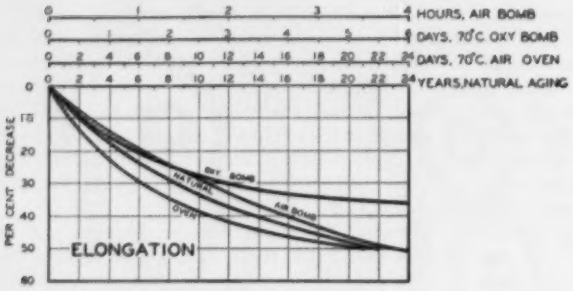


FIG. 4.—Elongation changes with natural and accelerated aging.

In evaluating the aging characteristics of a rubber compound, the changes in ultimate tensile and ultimate elongation properties are generally noted. Yet seldom, if ever, are rubber parts in service used at their ultimate tensile or elongation, and few rubber articles are taken out of service because of failure of ultimate tensile strength or elongation. Most rubber parts become unserviceable because of changes of modulus. The modulus change that takes place under different conditions of aging is depicted in Figure 5.

It is obvious that the compound aged under natural conditions continues to increase in modulus for approximately 12 years, at the end of which time there is a very gradual decrease of modulus.

TABLE II

ELONGATION EQUIVALENTS

Natural aging (years)	70° Oxygen bomb (days)	70° Air oven (days)	Air bomb (min.)
1	0.25	0.75	17
2	0.50	1.5	23
3	0.92	2.3	38
4	1.25	3.0	52
5	1.63	3.75	68
10	4.13	7.5	120
11		8.5	130
15		12.4	170
20		18.00	212
22		21.00	220

When aged in the oven, there is a fairly rapid change of modulus for the first 7 or 8 days, after which time a definite leveling takes place, so that, even after 21 days, the increase of modulus is equal only to that of approximately 6.5 years of natural aging. It is difficult to predict whether, with continued oven aging, the modulus increase would ever reach the values obtained for 12 years of natural aging.

In the oxygen bomb there is a rapid increase of modulus for the first 2 days, when there is a definite leveling, and after about 4 days there is a tendency to drop, so that in this instance the oxygen bomb can predict changes in modulus up to about 4.5 years. Beyond that point, further aging in the oxygen bomb is of no value in making correlations.

The air bomb causes the modulus to increase for about the first 1.25 hours, and exposure for longer periods causes a rapid deterioration of modulus. Ac-

cording to these figures, the compound would increase in modulus for about 3.5 years of natural aging, after which time there would be a decline of modulus. Continuing the exposure in the air bomb for 4 hours causes the percentage modulus increase to return to zero. This, of course, is not true of natural aging.

By comparing the various accelerated aging curves in Figure 5 with the natural aging curve, Table III is developed.

From the figures shown, it is obvious that not all the characteristics of a compound depreciate at the same rate under accelerated conditions, as they are under natural conditions. Therefore, a set of time intervals along the

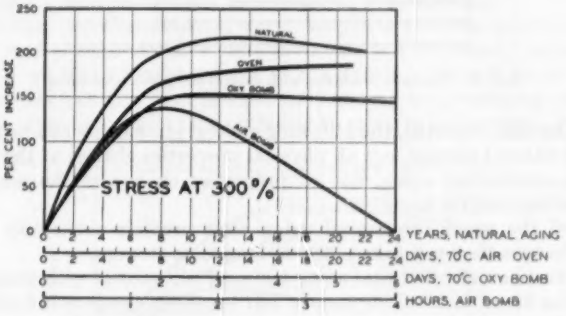


FIG. 5.—Modulus changes with natural and accelerated aging.

horizontal axis was devised which would permit superimposing the percentage tensile depreciation curves for all types of aging, as shown in Figure 6.

Using the same time intervals, the curve for elongation was developed, and is shown in Figure 7. No longer can these curves be superimposed on one another—an indication that the rate of tensile depreciation is not the same as the rate of elongation depreciation under all conditions of aging.

Similarly, the differences in rate of change of modulus are much more pronounced than the changes of elongation, as shown in Figure 8.

The air bomb causes the least modulus increase, the oxygen bomb more, and the oven the greatest, yet none approximates the change of modulus that takes place on natural aging. Of the three types of accelerated aging, the oven most nearly approximates the change that takes place in natural aging.

TABLE III

MODULUS EQUIVALENTS

Natural aging (years)	Oxygen bomb (days)	Oven aging (days)	Air bomb (min.)
1.0	0.4	1.2	14
2.0	0.75	2.4	25
3.0	1.25	4.1	45
3.5	1.55	4.8	57 or 110
4.0	1.80	5.5	—
4.5	2.30	6.4	—
5.0	—	7.5	—
5.5	—	10.0	—
6.0	—	14.0	—
6.5	—	21.0	—

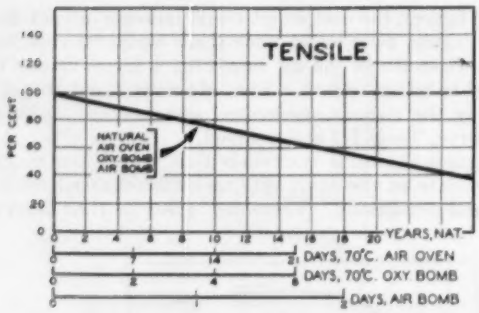


FIG. 6.—Tensile depreciation with natural and accelerated aging.

From the data reported, the following general statements can be made:

During natural storage, not all physical properties change at the same rate.

During accelerated aging, not all properties change at the same relative rates as during natural aging.

None of the usual accelerated aging tests predicts accurately all of the physical changes that will take place on long-time storage.

Of the three accelerated heat aging tests, all will predict with some degree of accuracy the trend in breaking tensile and breaking elongation during limited long-time storage.

Of the three types, the air bomb is least reliable for predicting modulus change at normal temperatures. The 70° oxygen bomb exposure is somewhat more reliable. The best method is the 70° circulating air oven. For this particular stock, it could be used for predicting shelf life yp to 6 years.

The oven test as introduced by Geer[5] was the first of the accelerated aging test methods to find wide acceptance. At that time (1916), 2 and 4 days in a 70° C oven caused considerable depreciation of the tensile properties of a normal compound.

As compounding techniques improved, longer and longer oven aging was necessary to deteriorate physical properties. To reduce the time necessary to deteriorate a compound, Bierer and Davis[6] introduced the oxygen bomb, which was recommended for use at 60° or 70° C and 300-pound oxygen pressure.

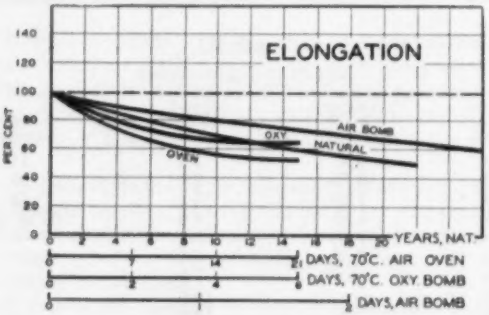


FIG. 7.—Elongation changes with natural and accelerated aging.

Exposure for hours under these conditions caused deterioration apparently equal to that requiring days in the air oven at 70° C. This represented a saving in aging time and the method found considerable favor. Later it was shown that the time to cause a given deterioration could be reduced roughly 50 per cent by raising the temperature to 80° C. This procedure found wide acceptance.

In the late 1920's, the air bomb[7] was introduced. This test, conducted at 127° C and 80-pound air pressure, was designed to simulate inner-tube service conditions. The conditions prescribed deteriorated compounds in hours to an extent which would normally take days in the oxygen bomb and possibly weeks in the air oven. It represented a further saving in aging time.

Despite that fact that this test was developed to simulate inner-tube service, it was adopted because it was a time saver and not necessarily because it had any bearing on the ultimate service of the article. Several branches of the rubber industry use this test method as a means for predicting service life, whereas the actual service of the article has no relation to the test. An extreme

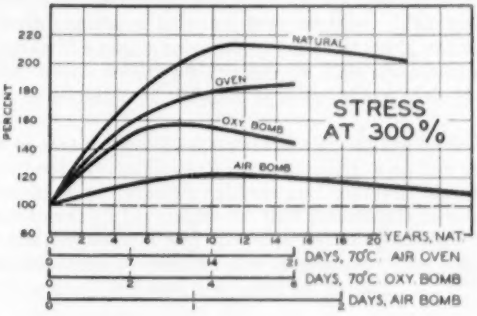


FIG. 8.—Modulus changes with natural and accelerated aging.

case is use of the air bomb for testing foam mattresses and pillows; this is only a heat deterioration test and not a measure of service life.

Any of the three aging methods can be used for predicting changes of breaking tensile and breaking elongation. However, most rubber items do not fail in service because of changes of ultimate tensile or ultimate elongation, but rather because of other changes, such as modulus. Yet, all too often, modulus changes are not given their proper consideration in evaluating anticipated service life of a compound.

For the compound being discussed, the air oven predicted natural shelf-life modulus changes for 6.5 years, the oxygen bomb for 4.5 years, and the air bomb for only 3.5 years. Each piece of apparatus, in the order named, reduces the time necessary to cause a certain percentage deterioration of properties. However, as the speed of deterioration increases, the length of time for which modulus changes can be forecast is reduced. So, the effort to become efficient by saving testing time defeats its purpose; eventually it becomes wasteful to run accelerated aging tests, the results of which do not forecast the service life of the article.

In selecting accelerated aging conditions, service conditions should be considered and aging conditions that most nearly approximate service conditions

should be used. From the data presented, it appears that the air oven is better than either the air bomb or oxygen bomb for predicting modulus changes. The more nearly service conditions are simulated, the more meaningful the tests become.

ACKNOWLEDGMENT

The authors wish to thank the R. T. Vanderbilt Company for permission to present this paper.

REFERENCES

[1] American Society for Testing Materials, "ASTM Standards for Rubber", Designation D412-51T.
[2] American Society for Testing Materials, "ASTM Standards for Rubber", Designation D856-51. In this ASTM specification, the test is designated as the "test-tube method", not as the "air oven test", as this test is called in the present paper. The term air oven test is customarily reserved for the long used single chambered oven of Geer (India Rubber World 55, 127 (1916)), which is described in ASTM Designation D573-53. [Ed.]
[3] American Society for Testing Materials, "ASTM Standards for Rubber", Designation D572-53.
[4] American Society for Testing Materials, "ASTM Standards for Rubber", Designation D454-53.
[5] Geer, *India Rubber World* **55**, 127 (1916).
[6] Bierer and Davis, *Ind. Eng. Chem.* **16**, 711 (1924).
[7] R. T. Vanderbilt Co., "Vanderbilt Rubber Handbook", edited by Rogers, New York, 1948, p. 454.

THE SHRINKAGE OF MOLD CURED ELASTOMER COMPOSITIONS *

A.E. JUVE AND J. R. BEATTY

THE B. F. GOODRICH RESEARCH CENTER, BRECKSVILLE, OHIO

INTRODUCTION

In the manufacture of molded products for certain applications, especially in the aeronautical and automotive industry, the dimensions of the finished part must be maintained within close tolerances. One of the factors which enters into this problem is that of shrinkage, which is defined in this report as the difference between the dimensions of a mold cavity and the product vulcanized in the cavity, both measured at room temperature. The term shrinkage is also used to describe the rearrangement of material, as in calendered sheets or extruded sections, which occurs on warming. This phenomenon, however, is not accompanied by a change of volume, as is shrinkage of molded articles, and is not considered here.

The purpose of this work is to compare the shrinkage of different compositions when vulcanized in a mold cavity, particularly with the view to compare the effect on shrinkage of different rubbers and different loading pigments at various concentrations. The results of this investigation are expressed by means of tables and graphs in a way that enables compounders to calculate the shrinkage of compositions of rubbers and pigments. The base recipes (pure gum) on which this study is based are listed in Table 1.

FACTORS AFFECTING SHRINKAGE

THERMAL CONTRACTION

It is generally recognized that the principal factor responsible for shrinkage is the thermal contraction resulting from cooling from the temperature of vulcanization to room temperature. Partly counteracting this change is the increase of dimensions of the mold cavity resulting from heating from room temperature to the temperature of vulcanization.

McPherson[1] published data on the thermal coefficient of expansion of a series of rubber stocks containing varying amounts of combined sulfur.

Later Scott[2] published data on a similar series, in which the rubber used was highly purified.

Powell[3] used a figure of 6.6×10^{-4}/° C as the coefficient of volume expansion for a high-gum mix, which agrees closely with the values reported by the Bureau of Standards, and pointed out that loaded stocks have a proportionately lower value of volume expansion. He also reported that reclaimed rubber or factice affected the shrinkage as rubber would.

Young[4] published a table showing the variation of shrinkage with hardness of the stocks, which demonstrated the variation of shrinkage with changes of

* Reprinted from the *Rubber World*, Vol. 131, No. 1, pages 62–8, October 1954.

loading, but he apparently did not recognize that shrinkage also depended on the curing temperature which was employed.

In a bulletin from the du Pont laboratories[5], shrinkage data are shown for a variety of stocks of Neoprene, GR-S, and natural rubber, in which the role of the curing temperature is well illustrated, as well as the effects of varying loadings of several pigments.

CHEMICAL EFFECTS OF VULCANIZATION

A second factor affecting the shrinkage is the change of volume resulting from vulcanization. This is small for the usual soft rubber vulcanizates, but

TABLE 1

BASIC RECIPES

Natural Rubber	
Natural rubber	100
Zinc oxide	5
MBT*	†0.6
Stearic acid	1
PBNA‡	1
Sulfur	3

GR-S	
GR-S 1001	100
Zinc oxide	5
CBS§	1
Sulfur	1.75

Butyl	
GR-I-15	100
Zinc oxide	5
Stearic acid	3
TMTD¶	1
MBTS‖	0.5
Sulfur	2

Hycar 1002 and 1001	
Polymer	100
Zinc oxide	5
MBTS‖	1.5
Sulfur	1.5

Neoprene GN	
Neoprene GN	100
Zinc oxide	5
Magnesium oxide	4

Neoprene W	
Neoprene W	100
Zinc oxide	5
Stearic acid	0.5
Magnesium oxide	2
TMTM**	0.5
Sulfur	1

Neoprene FR	
Neoprene FR	100
PBNA‡	2
Sublimed litharge	10
Sulfur	1

* Mercaptobenzothiazole.
† Adjusted upward for channel black and clay stocks.
‡ Phenyl-2-naphthylamine.
§ Santocure, *N*-cyclohexyl-2-benzothiazole sulfenamide, Monsanto Chemical Co., Rubber Service Department, Akron, O.
¶ Tetramethylthiuram disulfide.
‖ 2,2'-Dithiobis(benzothiazole).
** Tetramethylthiuram monosulfide.

becomes increasingly important as the sulfur ratio is increased. This factor was measured in hard-rubber cures by Glancy and coworkers[6], and accurate figures of the values for varying proportions of combined sulfur in simple sulfur-natural rubber stocks were reported by McPherson[1].

The dimensional change caused by the chemical reaction between natural rubber and sulfur was measured for stocks based on the gum recipe of Table 1, in which 1.5, 3.0, and 4.5 parts of sulfur were used, with suitable adjustments of the accelerator ratio. The shrinkage was measured directly and also calculated from the coefficient of expansion. The shrinkage due to curing agent-rubber combination is shown in Figure 1, and compared with data from the Bureau of Standards on simple rubber-sulfur compositions. Because of the

wide disparity between the two sets of data, a series of rubber-sulfur mixtures was made, and similar measurements checked closely with the Bureau of Standards data. The conclusion was reached that, for accelerated stocks, the shrinkage due to vulcanization is much less for equal quantities of combined sulfur than for simple rubber-sulfur mixes.

The shrinkage due to vulcanization for the three-part sulfur stock (2.8 per cent combined sulfur) is about 0.0009 inch/inch. For compounded stocks this would be reduced in proportion to the volume of rubber present. In the calculation of the shrinkages in Tables 3–7 inclusive, this factor has not been included for the reason that it is small and of about the order of the accuracy of the shrinkage measurements.

In the following procedures for the calculation of mold shrinkage from the recipe, no account is taken of this effect, However, for compositions containing proportions of sulfur higher than three parts, an allowance should be made

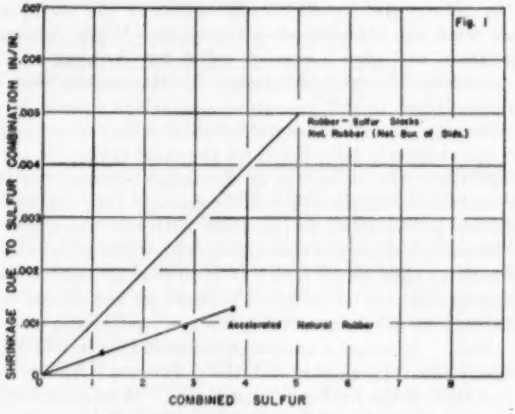


FIG. 1.—Effect of combined sulfur on shrinkage—accelerated and non-accelerated natural rubber stocks.

based on the data of Figure 1. It should be noted that this effect is independent of the curing temperature.

To our knowledge no data have been published on the extent of this effect with GR-S sulfur vulcanizates, with nitrile rubber-sulfur vulcanizates, or on the reduction of volume accompanying a conventional Neoprene cure.

OTHER FACTORS

In a study of the precision with which a rubber-metal structure could be produced, the British Ministry of Supply[7] published some useful data concerning shrinkage. The part played by thermal contraction and volume change due to sulfur combination were investigated. Also the complicating effects of grain direction were studied, and the special effects which occur in rubber-metal structures were recognized.

The complicating effect of grain direction mentioned above is a factor which frequently causes trouble in practice. In a stock which has a high degree of orientation introduced by calendering or extrusion, the difference in shrinkage

between the two directions, i.e., parallel to and across the direction of the grain, is very marked, i.e., large in the transverse direction and small in the longitudinal direction.

Although no compounds containing reclaimed rubber were included in this study, experience has shown that, in calculating the shrinkage of such compounds, the rubber hydrocarbon value plus the acetone extract (the latter calculated as having a density of 1.00) may be added to the rubber value of the compound, and the presence of pigment which may appear in the reclaim may be neglected.

Fibrous materials such as cotton linters, ground friction scrap, or asbestos fibers, when present, cause some complications. Since processing operations such as calendering or extrusion tend to orient the fibers, the resulting stock may have a very much greater shrinkage in the direction perpendicular to the fibers than in the parallel direction. Also the retarding effect on shrinkage of the fibrous materials is greater than that of clay. No data on such stocks are included in this report, and actual measurements of the shrinkage are recommended rather than an attempt at calculation. While measurements of a cross-plied specimen will give a correct value for shrinkage, it is difficult to apply these measurements to mold design for the reason that the extent of orientation accomplished in the processing operations cannot be predicted.

A similar difficulty, except on a smaller scale, occurs in normal stocks. If a high degree of orientation is introduced by the most favorable (or unfavorable) calendering conditions, the difference in shrinkage between the two directions, i.e., parallel to and across the direction of the grain, is very marked. This makes it difficult in some applications to calculate with any accuracy the shrinkage allowance for the mold, since the operations which introduce the grain are less susceptible of control than those which control the normal shrinkage.

A few comments should be included concerning the effects of shrinkage in products containing metal parts which have low coefficients of expansion compared to the rubber. In a metal sandwich construction in which a layer of rubber is vulcanized to two sheets of metal, the difference between the contraction of the metal and that of the rubber is quite large. Also contraction of the rubber in the two directions parallel to the metal surfaces is prevented by the attachment of the rubber to the metal. Thus most of the contraction must take place in the direction perpendicular to the metal surfaces. If the rubber thickness is relatively small and the area of the plates large, the contraction in thickness of the rubber layer approaches three times the normal linear contraction. In most products this condition is not approached, so that the shrinkage of the rubber layer varies, depending on a shape factor from one to three times the normal linear shrinkage. One result of this condition is that the rubber of such composite structure may be quite highly stressed and thus may contribute to premature failures.

TEST EQUIPMENT AND PROCEDURES

The test sample used in this work is illustrated in Figure 2. The samples were constructed by plying up four milled sheets with the grain of alternate plies at right angles to minimize the grain effect. Commercial grades of polymers and pigments were used, and cures were adjusted on the basis of optimum cures selected from stress-strain tests. Curing temperatures were 140° C for natural rubber stocks and 150° C for synthetic rubber stocks.

The raised portion of the specimen (inner rectangle), Figure 2, has nominal

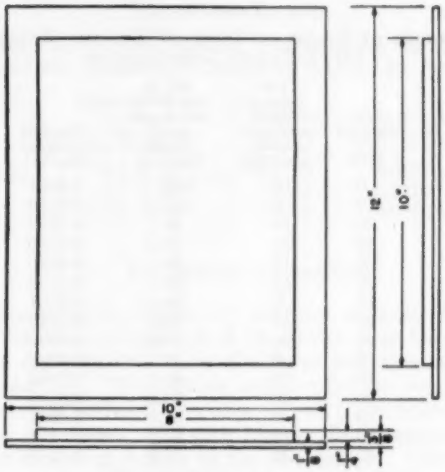


FIG. 2.—Test sample dimensions.

dimensions of eight by ten inches. These dimensions were measured for shrinkage. It was assumed that the thickness would change in the same proportion as length and width. The dimensions of the mold were machined to an accuracy of ±0.0002, measured with gauge blocks at room temperature.

Shrinkage measurements were made by two means, a micrometer caliper and a cathetometer at a room temperature of 25° C. The two measurements agreed in all cases, and only the micrometer caliper data are reported. The shrinkage is expressed in inches/inch.

In several instances the linear coefficient of expansion was measured directly by use of a temperature controlled air oven with a glass lid, so that measurements of length and width of the test-piece could be made at various temperatures by means of a cathetometer. The test-piece was dusted with talc, so dimensional changes would not be restrained by forces resulting fromcon tact with the polished stainless steel plate supporting it. Measurements were made at 25, 45, 70, and 100° C, and in some cases at 125° C. The slope of the best fitting straight line through the four (or five) points gives the coefficient of linear expansion directly. These data (see Table 2) were used for calculations to check the shrinkage measurements.

TABLE 2

LINEAR COEFFICIENTS OF EXPANSION OF RUBBERS IN BASE RECIPES

Rubber	Coefficient of expansion
Natural	220×10^{-6} in./in./° C
GR-S	221×10^{-6} in./in./° C
Low-temperature polymerized	221×10^{-6} in./in./° C
Nitrile, Hycar 1002	195×10^{-6} in./in./° C
1001	199×10^{-6} in./in./° C
Neoprene GN	206×10^{-6} in./in./° C
W	196×10^{-6} in./in./° C
FR	200×10^{-6} in./in./° C
Butyl, GR-I-15	194×10^{-6} in./in./° C

TABLE 3

SUMMARY OF SHRINKAGE DATA ON NATURAL RUBBER, 140° C CURING TEMPERATURE

Recipe variation*	Vols. pigment 100 PHR	Vols. pigment 100 V rubber + organic materials	Vol. % rubber + sulfur and other organic materials	Measured shrinkage (in./in.)	Corrected calculated shrinkage (in./in.)
None	0	0	100	0.0231	0.0238
Coarse whiting	10	9	91.2	0.0199	0.0199
	20	18	84.1	0.0179	0.0179
	40	36	73.3	0.0156	0.0156
Pptd. whiting	20	18	84.1	0.0189	0.0179
Ultrafine whiting	20	18	84.1	0.0183	0.0179
Fine clay	10	9	91.1	0.0161	0.0161
	20	18	84.1	0.0142	0.0141
	40	36	73.5	0.0099	0.0099
EPC black	10	9	91.1	0.0203	0.0203
	20	18	84.1	0.0184	0.0184
	40	36	73.3	0.0151	0.0156
Zinc oxide	10	9	91.1	0.0202	0.0202
	20	18	84.1	0.0177	0.0177
	40	36	73.3	0.0142	0.0142

The data above were used to draw Figure 3. The values in Column 6 below were computed from the coefficient of expansion of the base recipe and the suitable pigment correction factor scaled from Figure 3. Comparison of the values of Columns 6 and 5 show the agrement of measured and calculated shrinkage.

FEF black	20	18	84.1	0.0175	0.0184
HAF black	20	18	84.1	0.0177	0.0184
SWF black	20	18	84.1	0.0180	0.0184
FT black	20	18	84.1	0.0181	0.0184
MT black	20	18	84.1	0.0175	0.0184
EPC black + 10 PHR paraffin-base oil	20	16.6	85.0	0.0189	0.0188
EPC black + 20 PHR paraffin-base oil	20	14.9	87	0.0187	0.0189
EPC black + 40 PHR paraffin-base oil	20	12.8	89	0.0185	0.0195
EPC black + 10 PHR fatty acid ester	20	16.5	85.4	0.0191	0.0188
EPC black + 10 PHR tributoxy-ethyl phosphate	20	16.6	85.2	0.0183	0.0187
EPC black + 5 PHR rosin + 5 PHR mineral oil	20	16.6	85.2	0.0196	0.0187
EPC black + 10 PHR soft Cumar	20	16.6	85.2	0.0195	0.0187
EPC black + 10 PHR pine tar	20	16.6	85.2	0.0202	0.0187
EPC black + 10 PHR petrolatum	20	16.5	85.6	0.0190	0.0188
EPC black + 10 PHR mineral rubber	20	16.6	85.2	0.0183	0.0187
EPC black + 10 PHR petrolatum cured with TMTD	20	16.3	85.6	0.0201	0.0188

* See Table 1 for base recipe.

TABLE 3 (continued)

SHRINKAGE OF NATURAL RUBBER COMPOSITIONS CONTAINING 40 VOLUMES PIGMENT/100 PARTS BY WEIGHT OF RUBBER

Pigment	Pigment coefficient of linear expansion (in./in./8° C)	Base line shrinkage (in./in.)	Theoretical shrinkage (in./in.)	Measured shrinkage (in./in.)
Channel black	5.5×10^{-6}	0.0175	0.0177	0.0151
Whiting	10.0×10^{-6}	0.0175	0.0178	0.0156
Zinc oxide	3.55×10^{-6}	0.0175	0.0176	0.0142

EXPRESSION OF RESULTS

The results are given in Tables 3–7 and the corresponding Figures 3–7. Explanation of the column headings of the tables is as follows. The recipe variations of the compositions whose shrinkage was measured are shown in Column 1 of Tables 3–7. This column includes (a) the base recipe; (b) compositions with pigment added to the base recipe; (c) compositions of the base recipe + pigment + softener. Column 2 shows the volumes of pigment added per 100 parts by weight of rubber to the base recipe. Column 3 shows the ratio of volumes of pigment per 100 volumes of rubber + organic materials. Column 4 is the volume percentages of rubber + sulfur + other organic materials which are used in calculations of shrinkage (see formula below). Column 5 is the measured shrinkage of the vulcanized rubber sample. (Rubber sample and mold at room temperature, 25° C). Column 6 is the corrected calculated shrinkage computed in the following manner:

Shrinkage = (coefficient of expansion of base recipe − coefficient of expansion of mold steel) × temperature change from curing to room temperature × per cent rubber, sulfur, and softeners less a pigment correction factor determined from the difference between the expected or theoretical shrinkage and the actual shrinkage.

The base line on Figures 3–7 is the shrinkage based on the assumption that the pigment has no effect on the shrinkage of the mixture. It might be expected that the theoretical shrinkage of a mixture of a rubber and a pigment would be the sum of the coefficients of the two materials corrected for their volume concentrations and the temperature change. In nearly all cases, however, the measured shrinkage of such mixtures is much less than these values. Table 3 shows some typical theoretical shrinkages compared to the base line shrinkages, showing that, for practical purposes, no serious error is introduced by assuming them to be equivalent. This is convenient, for information of the coefficients of thermal expansion of pigments is not well known. It is also shown that the measured shrinkage is much less than either the base line or theoretical shrinkage.

Thus, most of the pigments were found to have a retarding effect on shrinkage above that which would be expected. This indicates that the pigment is preventing the rubber from shrinking as much as it otherwise would.

DISCUSSION OF RESULTS

NATURAL RUBBER

Table 3 shows the data for natural-rubber stocks, with and without various loading pigments and softeners. Figure 3 shows the effect of some of the more

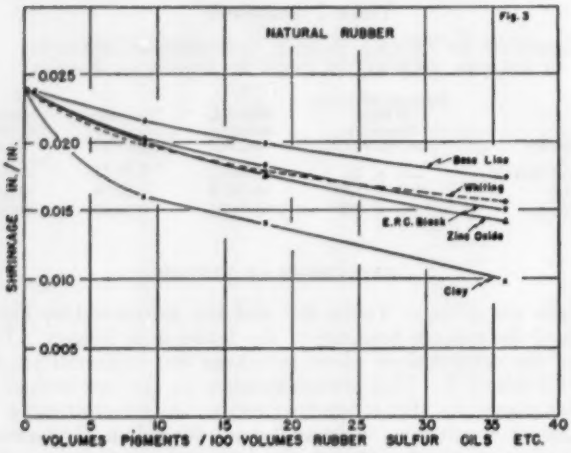


FIG. 3.—Effect of volume of pigment on shrinkage of natural rubber.

common pigments at loadings of 10, 20, and 40 volumes per 100 parts by weight of rubber.

Clay markedly decreased the shrinkage, while zinc oxide, whiting, and channel black decreased it slightly. Softeners, as mentioned above, increase the shrinkage in direct proportion to the volume used, as though an equal volume of rubber had been added.

No significant difference could be noted when tetramethylthiuram disulfide was used as the curing agent in place of sulfur.

Carbon blacks, which varied widely in particle size and reinforcing power, were found to have essentially equal effects on shrinkage, as shown in Table 8.

TABLE 4

SUMMARY OF SHRINKAGE DATA ON GR-S, 150° C CURING TEMPERATURE

Recipe variation*	Vols. pigment 100 PHR	Vols. pigment 100 V rubber + organic materials	Vol. % rubber + sulfur and other organic materials	Measured shrinkage (in./in.)	Corrected calculated shrinkage (in./in.)
None	0	0	100	0.0268	0.0262
Ultrafine whiting	20	18.5	84	0.0214	0.0220
Pptd. whiting	20	18.5	84	0.0226	0.0220
Coarse whiting	10	9.25	91	0.0238	0.0238
	20	18.5	84	0.0220	0.0220
	40	37	73	0.0181	0.0181
Fine clay	10	9.25	91	0.0216	0.0216
	20	18.5	84	0.0181	0.0181
	40	37	73	0.0126	0.0126
EPC black	10	9.25	91	0.0246	0.0246
	20	18.5	84	0.0216	0.0216
	40	37	73	0.0152	0.0152
Zinc oxide	10	9.25	91	0.0244	0.0244
	20	18.5	84	0.0220	0.0220
	40	37	73	0.0183	0.0183

TABLE 4 (continued)

The data above were used to draw Figure 4. The values in Column 6 below were computed from the coefficient of expansion of the base recipe and the suitable pigment correction factor scaled from Figure 4. Comparison of the values of Columns 6 and 5 show the agreement of measured and calculated shrinkage.

FEF black	20	18.5	84	0.0211	0.0216
HAF black	20	18.5	84	0.0211	0.0216
SRF black	20	18.5	84	0.0217	0.0216
MT black	20	18.5	84	0.0217	0.0216
FT black + 10 PHR paraffin-base oil	20	16.7	85	0.0226	0.0220
HAF black + 10 PHR paraffin-base oil	20	16.7	85	0.0216	0.0220
EPC black + 10 PHR paraffin-base oil	20	16.7	85	0.0214	0.0220
EPC black + 20 PHR paraffin-base oil	20	15.3	87	0.0226	0.0227
EPC black + 40 PHR paraffin-base oil	20	13	88.8	0.0224	0.0231
FEF black + 10 PHR paraffin-base oil	20	16.7	85	0.0212	0.0220
SRF black + 10 PHR paraffin-base oil	20	16.7	85	0.0210	0.0220
EPC black + 10 PHR fatty acid ester	20	16.7	85	0.0215	0.0220
EPC black + 10 PHR tributoxy-ethyl phosphate	20	16.7	85	0.0222	0.0220
EPC black + 5 PHR rosin + 5 PHR mineral oil	20	16.7	85	0.0214	0.0220
EPC black + 10 PHR soft Cumar	20	16.7	85	0.0212	0.0220
EPC black + 10 PHR mineral rubber	20	16.7	85	0.0208	0.0220
EPC black + 10 PHR petrolatum	20	16.7	85	0.0214	0.0213
EPC black + 10 PHR pine tar	20	16.7	85	0.0214	0.0213

* See Table 1 for base recipe.

GR–S

The data for GR-S stocks containing various loading pigments and softeners are summarized in Table 4. Figure 4 shows the effect of some common pigments on shrinkage.

Clay and EPC black decrease the shrinkage appreciably, while whiting and zinc oxide show only a slight effect. In general, GR-S behaves with the various pigments and softeners as does natural rubber. Low-temperature polymerized GR-S behaves the same as standard GR-S.

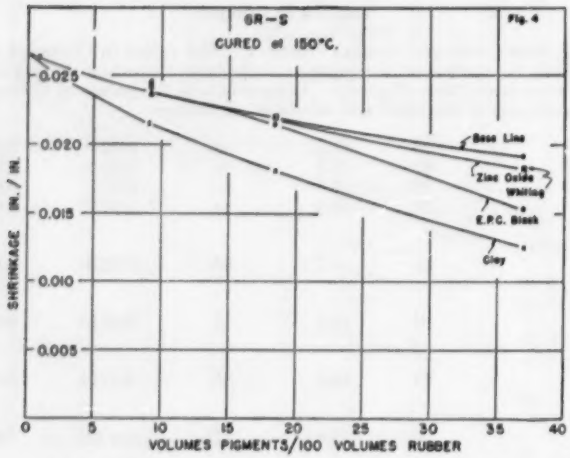


FIG. 4.—Effect of volume of pigment on shrinkage of GR-S.

NITRILE RUBBER

Table 5 shows the data for Hycar 1002 nitrile rubber[8] stocks. Loading pigments appear to retard the shrinkage of these stocks less than with other elastomers, as shown in Figure 5. Clay, however, has the greatest effect. Resins such as Durez-12687[9] and Goodrite Resin-50[8] behave essentially as if they were rubber. The ester-type plasticizers increase the shrinkage more than

TABLE 5

SUMMARY OF SHRINKAGE DATA ON NITRILE RUBBER—HYCAR 1002, 150° C CURING TEMPERATURE

Recipe variation*	Vols. pigment 100 PHR	Vols. pigment 100 V rubber + organic materials	Vol. % rubber + sulfur and other organic materials	Measured shrinkage (in./in.)	Corrected calculated shrinkage (in./in.)
None	0	0	100	0.0231	0.0229
None—Hycar 1001	0	0	100	0.0228	0.0232
Hycar 1001 + EPC black	20	19.3	83	0.0189	—
Coarse whiting	10	9.65	90.4	0.0206	0.0206
	20	19.3	83	0.0188	0.0186
	40	38.6	72	0.0160	0.0160
Pptd. whiting	20	19.3	83	0.0197	0.0188
Ultrafine whiting	20	19.3	83	0.0201	0.0188
Fine clay	10	9.65	90.4	0.0206	0.0206
	20	19.3	83	0.0176	0.0176
	40	38.6	72	0.0136	0.0136
EPC black	10	9.65	90.4	0.0200	0.0200
	20	19.3	83	0.0185	0.0185
	40	38.6	72	0.0146	0.0146
Zinc oxide	10	9.65	90.4	0.0202	0.0202
	20	19.3	83	0.0181	0.0181
	40	38.6	72	0.0143	0.0143

TABLE 5 (continued)

The data above were used to draw Figure 5. The values in Column 6 below were computed from the coefficient of expansion of the base recipe and the suitable pigment correction factor scaled from Figure 5. Comparison of the values of Columns 6 and 5 show the agreement of measured and calculated shrinkage.

FEF black	20	19.3	83	0.0175	0.0185
HAF black	20	19.3	83	0.0176	0.0185
SRF black	20	19.3	83	0.0187	0.0185
FT black	40	38.6	72	0.0161	0.0146
MT black	40	38.6	72	0.0157	0.0146
Durez 12687 Resin, 20 PHR	0	0	100	0.0222	0.0229
Durez, 40 PHR	0	0	100	0.0214	0.0229
Goodrite Resin 50, 10 volumes	0	0	100	0.0215	0.0229
Goodrite Resin 50, 20 volumes	0	0	100	0.0213	0.0229
Goodrite Resin 50, 40 volumes	0	0	100	0.0224	0.0229
EPC black + 20 PHR tributoxyethyl phosphate	20	16.3	86	0.0216	0.0197
EPC black + 20 PHR dioctyl phthalate	20	16.3	86	0.0224	0.0197
EPC black + 20 PHR soft Cumar	20	16.3	86	0.0204	0.0197
EPC black + 20 PHR soft coal tar	20	16.3	86	0.0198	0.0197
EPC black cured with TMTD	20	19.3	83	0.0190	0.0185

* See Table 1 for basic recipe.

if they are considered as rubber; while soft coal tar and coumarone behave as rubber, but also effectively cancel the retarding effect of the pigment. Again no difference could be found between a tetramethylthiuram disulfide cure and a normal sulfur cure. Different types of black had the same effect on shrinkage.

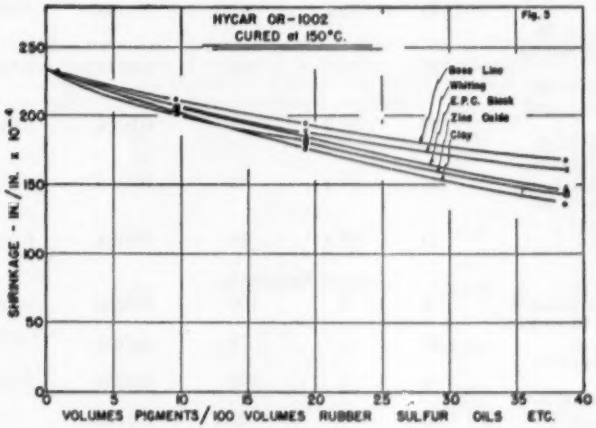


FIG. 5.—Effect of volume of pigment on shrinkage of nitrile rubber.

Hycar 1001 in a gum stock and a 20-volume black loaded stock gave shrinkage values identical with those of Hycar 1002.

NEOPRENE

The results obtained with Neoprene GN[10] are summarized in Table 6, and the effects of pigments on the shrinkage are shown in Figure 6. This effect is large for all pigments, with clay having the greatest effect for the one loading tested. Softeners behave as rubber, and all the blacks are equivalent.

TABLE 6

SUMMARY OF SHRINKAGE DATA ON NEOPRENE GN, 150° C CURING TEMPERATURE

Recipe variation*	Vols. pigment 100 PHR	Vols. pigment 100 V rubber + organic materials	Vol. % rubber + sulfur and other organic materials	Measured shrinkage (in./in.)	Corrected calculated shrinkage (in./in.)
None	0	0	100	0.0236	0.0243
Coarse whiting	20	24	80.5	0.0154	
Pptd. whiting	20	24	80.5	0.0164	
Fine clay	20	24	80.5	0.0114	
EPC black	10	12	87	0.0172	0.0172
	20	24	80.5	0.0154	0.0154
	40	48	67.5	0.0129	0.0129
Zinc oxide	20	24	80.5	0.0150	

The data above were used to draw Figure 6. The values in Column 6 below were computed from the coefficient of expansion of the base recipe and the suitable pigment correction factor scaled from Figure 6. Comparison of the values of Columns 6 and 5 show the agreement of measured and calculated shrinkage.

FEF black	20	24	80.5	0.0154	0.0154
SRF black	20	24	80.5	0.0161	0.0154
FT black	20	24	80.5	0.0161	0.0154
MT black	20	24	80.5	0.0161	0.0154
EPC black + 10 PHR processing oil	20	21.2	82.5	0.0168	0.0160
EPC black + 20 PHR processing oil	20	19.1	84	0.0174	0.0164
EPC black + 10 PHR fatty acid ester	20	21.3	82	0.0166	0.0160
EPC black + 10 PHR tributoxyethyl phosphate	20	21.4	82	0.0166	0.0160
EPC black + 10 PHR dioctyl phthalate	20	21.3	82	0.0163	0.0160
		Other Neoprenes			
None—Neoprene W	0	0	100	0.0226	0.0231
Neoprene W + EPC black	20	—	79	0.0162	—
None—Neoprene FR	0	0	100	0.0258	0.0238
Neoprene WF + EPC black	20	—	82.3	0.0175	—

* See Table 1 for basic recipe.

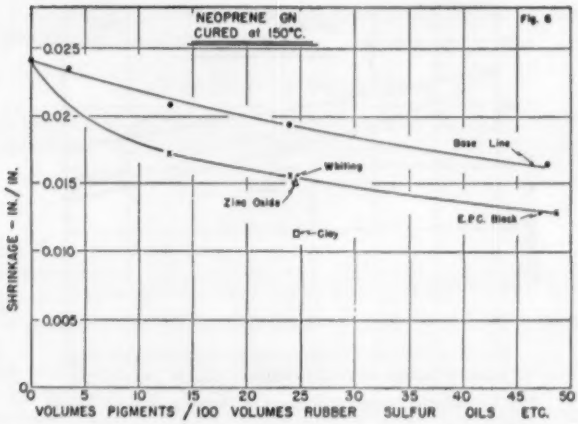


FIG. 6.—Effect of volume of pigment on shrinkage of Neoprene rubber.

TABLE 7

SUMMARY OF SHRINKAGE DATA ON GR-I-15—BUTYL RUBBER, 150° C CURING TEMPERATURE

Recipe variation*	Vols. pigment 100 PHR	Vols. pigment 100 V rubber + organic materials	Vol. % rubber + sulfur and other organic materials	Measured shrinkage (in./in.)	Corrected calculated shrinkage (in./in.)
None	0	0	100	0.0236	0.0228
Pptd. whiting	20	17.5	85	0.0166	0.0166
Fine clay	20	17.5	85	0.0140	0.0140
EPC black	10	8.75	92	0.0181	0.0181
	20	17.5	85	0.0164	0.0164
	40	35	74	0.0126	0.0126
Zinc oxide	20	15.9	86.5	0.0162	0.0167

The data above were used to draw Figure 7. The values in Column 6 below were computed from the coefficient of expansion of the base recipe and the suitable pigment correction factor scaled from Figure 7. Comparison of the values of Columns 6 and 5 show the agreement of measured and calculated shrinkage.

FEF black	20	17.5	85	0.0166	0.0164
SRF black	20	17.5	85	0.0161	0.0164
FT black	20	17.5	85	0.0164	0.0164
EPC black + 10 parts paraffin base oil	20	15.9	86.5	0.0162	0.0167
EPC black + 20 parts paraffin base oil	20	14.6	87.5	0.0172	0.0173
EPC black + 10 parts fatty acid ester	20	16.1	86	0.0166	0.0169
EPC black + 20 parts fatty acid ester	20	14.7	86.5	0.0176	0.0167

* See Table 1 for basic recipe.

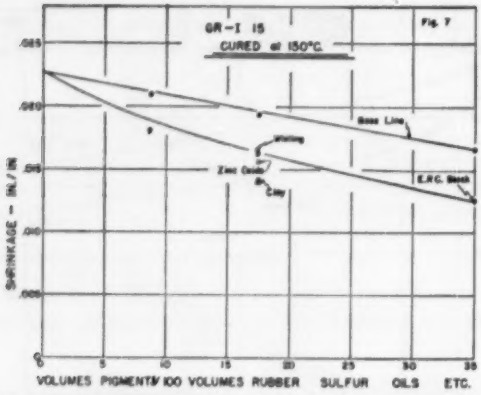


FIG. 7.—Effect of volume of pigment on shrinkage of Butyl rubber.

Neoprene W[10] in a gum stock and a 20-volume EPC black stock has about the same shrinkage as Neoprene GN. Neoprene FR has slightly higher shrinkage than GN.

BUTYL

Table 7 summarizes the data for shrinkage of Butyl compounds. Figure 7 shows the effect of pigments. Clay again decreases the shrinkage markedly. The various blacks behave similarly, and softeners behave as rubber.

VALIDITY OF RESULTS

Errors in the determinations arise from the following sources:

Errors in the curing temperature—not over ±1° C.

Recording of room temperature—not over ±0.5° C.

Measurements by micrometer or cathetometer—not over ±0.001 inch.

The maximum error probably does not exceed ±5 per cent when the above errors are additive.

Earlier work had shown that, in calculating the shrinkage from the recipe, all organic materials, such as accelerators, antioxidants, oils, and waxes as well as the sulfur present, could be considered as rubber in the calculation. For

TABLE 8

EFFECT OF CARBON BLACKS ON SHRINKAGE. 20 VOLUMES BLACK/100 PARTS BY WEIGHT OF POLYMER

	Shrinkage (in./in.)				
Black	Natural rubber*	GR-S	Neoprene GN	Hycar 1002	GR-I-25
EPC	0.0184	0.0216	0.0154	0.0185	0.0164
HAF	0.0177	0.0211	—	0.0176	—
SRF	0.0180	0.0217	0.0161	0.0187	0.0161
FEF	0.0175	0.0211	0.0154	0.0175	0.0166
FT	0.0181	—	0.0153	—	0.0164
MT	0.0175	0.0217	0.0161	—	—

* Cured at 140° C; all others at 150° C.

this reason, in the tables of data, the column showing the percentage of rubber by volume includes all these materials.

CALCULATION OF SHRINKAGE

In calculating the shrinkage of a composition from its recipe, the following formula applies when loading pigments are not present. (Base line shrinkage.)

$$S = \Delta T(C_1 - C_2)R$$

where

S = shrinkage in inches/inch

ΔT is the temperature difference between the curing temperature and room temperature in ° C

C_1* is the coefficient of thermal expansion of the gum stock (inches/inch ° C)

C_2 is the coefficient of thermal expansion of the mold material (11.5×10^{-6} inches/inch/° C for steel)

R is the percentage by volume of the rubber, sulfur + all organic materials.

* See Table 2.

When a loading pigment or a combination of loading pigments is present, the above formula must be modified by subtracting the correction for the retardation due to the pigments scaled from the curves of Figure 3–7. When two pigments are present, the contributions of each are added. Since the curves shown are for curing temperatures of 140° C for natural rubber stocks and 150° C for the synthetic stocks, the correction found must be adjusted for the actual curing temperature which is to be employed. Thus, if the correction turns out to be 0.0056 inch/inch, as scaled from the chart for natural rubber (140° C), and the desired curing temperature is 160° C, it would be corrected for the higher curing temperature by multiplying it by the factor:

$$\frac{160 - 25}{140 - 25}$$

where room temperature is 25° C, thus giving a corrected value of 0.0066 inch/inch. Only the most common pigments have been studied. For others, actual measurements must be made.

It was mentioned above that ester-type plasticizers with Hycar nitrile rubbers cause shrinkages greater than would be anticipated if the plasticizer is considered as rubber. For compositions such as these, the above calculation procedure will give erroneous results, and, in the absence of more complete data, actual shrinkage measurements should be made.

SUMMARY AND CONCLUSIONS

The coefficient of expansion of elastomer compositions depends on the kind of polymer employed, the volume per cent of polymer plus all other organic materials, and the kind and the amount of pigment present. The specific effects of pigments in retarding the shrinkage are shown.

A procedure is given by which the shrinkage of most soft rubber compositions of the principal rubbers may be calculated from the recipe.

The major part of the shrinkage of elastomer compositions is due to the much greater thermal contraction of the composition than of the material from

which the mold is made. This portion of the shrinkage depends on the thermal coefficient of expansion of the composition and the mold material and the temperature difference between the curing temperature and room temperature.

A minor part of the shrinkage is due to a contraction of volume resulting form vulcanization. For normal soft rubber stocks with sulfur ratios of three parts or less and for normal Neoprene stocks, this factor may be neglected. For stocks having higher sulfur ratios, an allowance needs to be made for this factor.

REFERENCES

[1] McPherson, National Bureau of Standards, Scientific Paper No. **560**, Part I, Aug. 1927.
[2] Scott, *J. Research Natl. Bur. Standards* **14**, 99 (1935).
[3] Powell, *Trans. Inst. Rubber Ind.* **20**, 2, 42 (1944).
[4] Young, *Rubber Age* (London) **24**, 227 (1943); **24**, 255 (1944).
[5] E. I. du Pont de Nemours & Co., Bulletin BL-208, **1946**.
[6] Glancy, Wright, and Oon, *Ind. Eng. Chem.* **18**, 73 (1926).
[7] Users' Memorandum U-14, Part 2, "Dimensional Stability and Thermal Expansion of a Particular Natural-Rubber Compound", British Ministry of Supply, Advisory Services on Plastics and Rubber, C.R.D. 46, London NW 1, England.
[8] Manufactured by the B. F. Goodrich Chemical Co., Cleveland, O.
[9] Manufactured by Durez Plastics & Chemicals, Inc., North Tonawanda, N. Y.
[10] Manufactured by E. I. du Pont de Nemours & Co.

TEMPERATURE CONTROL DURING MIXING OF RUBBER COMPOUNDS *

FRANK L. ROTH, GEORGE E. DECKER, AND ROBERT D. STIEHLER

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

It is well known that the properties of natural rubber vulcanizates are dependent on the temperature of the compound during the mixing process[1]. Schade and Roth[2] noted that the properties of synthetic rubber compounds and of the resulting vulcanizates also depended on the mixing temperature. This effect of mixing temperature is recognized in the Specifications for Government Synthetic Rubbers[3] and ASTM Designation D15-52T[4], both of which prescribe limits for the temperature of the mill roll surfaces during mixing.

Even though these limits permit a range of 18° or 20°F in the surface temperature, it is difficult to maintain the required temperature control because the rate of heat transfer through the conventional thick-walled roll is too slow. Part of the variations in results within and among laboratories is undoubtedly caused by variability in the temperatures of the rubber compounds during mixing.

At the request of the Office of Synthetic Rubber, the effect of mixing temperatures on the properties of GR-S vulcanizates and various means of controlling the temperature during mixing have been under investigation at the National Bureau of Standards during the last ten years. Two methods of control were considered: (1) keeping the rubber compound at a constant temperature throughout the mixing procedure, and (2) keeping the surfaces of the mill rolls at a constant temperature. In the first method of control a suitable sensing element and means to effect rapid changes in the temperature of the rolls would be essential. Since the achievement of such a control did not appear feasible, efforts were directed toward the second method.

EFFECT OF MIXING TEMPERATURE

The following compound was mixed on a mill having roll surfaces at temperatures of 100°, 120°, and 140° F in early studies in 1945.

Ingredient	Parts by weight
GR-S X-179	100
Channel Black	50
Softener (coal tar)	5
Zinc oxide	5
Sulfur	2
Mercaptobenzothiazole	1.5
Total	163.5

The mixing procedure was the same at each temperature. The temperature of the roll surfaces was measured with a surface pyrometer and was manually

* Reprinted from the *Rubber World*, Vol. 132, No. 4, pages 482–486, July 1955.

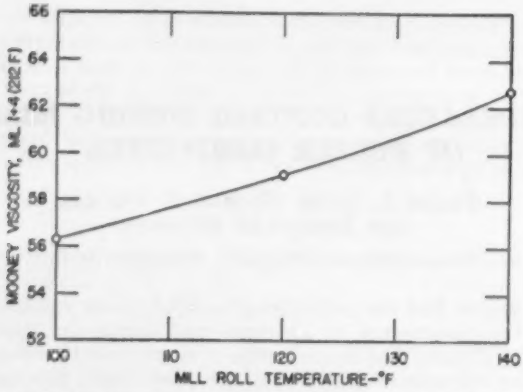


FIG. 1.—Effect of surface temperature of mill rolls on Mooney viscosity of a GR-S compound. Each point is the average of three mixes prepared on different days.

controlled within 5°F of the desired temperature throughout the mixing process. Three batches were mixed at each temperature.

The Mooney viscosity of the compounds is given in Figure 1. It is seen that the Mooney viscosity of the compound increased about six units for an increase in roll surface temperature from 100° to 140° F.

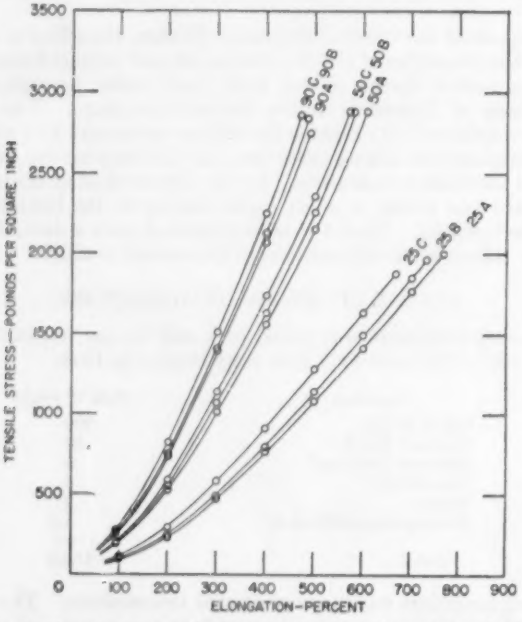


FIG. 2.—Effect of surface temperature of mill rolls on stress-strain properties of a GR-S compound. The numerals 25, 50, and 90 indicate the cure in minutes at 292° F, and the letters A, B, and C refer, respectively, to temperatures of 100°, 120°, and 140° F for the surfaces of the mill rolls during mixing of the compound.

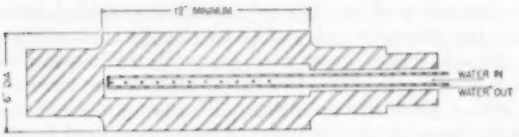


FIG. 3.—Central cavity mill roll. The diameter of the central cavity may vary from about 1¼ to 2 inches.

The tensile stress vs. elongation curves of vulcanizates cured 25, 50, and 90 minutes at 292° F are given in Figure 2. An increase of roll surface temperature resulted in an increase of stiffness and a decrease of elongation at failure. The increase of stress at 300 per cent elongation was about 3 lb. per sq. in. per degree Fahrenheit for all levels of cure. The decrease of ultimate elongation was greatest for the shortest cure and least for the longest cure. The effect of mixing temperature on stress at failure was not significant. The results of this study indicated that GR-S compounds, like those of natural rubber, require temperature control during mixing if reproducible values for their properties are to be obtained.

MILL ROLLS DESIGNS—NEW AND OLD

Most of the nominal 6 × 12-inch laboratory mill rolls are constructed like the design shown in Figure 3. The thickness of the walls is two inches or more, and cooling is obtained by spraying water against the inner walls. This arrangement results in a rate of heat transfer that is too slow to control the temperature of the surfaces within a few degrees.

ONE-INCH WALL ROLLS

The first attempt to increase the rate of heat transfer was the construction of rolls like the design in Figure 3, except for a reduction of wall thickness to one inch. The rate of heat transfer of these rolls was much greater than that of conventional rolls, but still insufficient to obtain the desired control of temperature of the roll surfaces.

SPIRAL GROOVED ROLLS

The next roll studied is shown schematically in Figure 4. This roll, developed by a rubber machinery manufacturing company, consists of three principal parts: (1) a mandrel about 4⅜ inches in diameter, having a central cavity 1¼ inches in diameter and two semicircular spiral grooves $\frac{5}{16}$ inch in

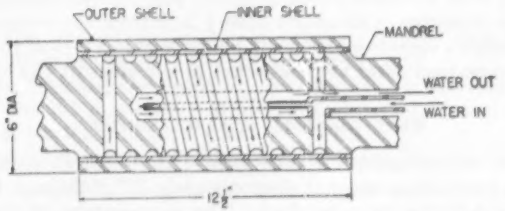


FIG. 4.—Commercial spiral-grooved mill roll, with improved heat-transfer characteristics.

radius cut into the outer surface; (2) a cylindrical inner shell $\frac{3}{16}$ inch in thickness, which fits over the mandrel and makes two continuous ducts of the spiral grooves; and (3) a hardened outer shell $\frac{1}{2}$ inch in thickness, which forms the working surface of the roll. The two spiral grooves are similar to a double-screw thread with a pitch of two inches. The two grooves are connected at one end by a hole diametrically through the mandrel to form a continuous duct. Part of the circulating fluid enters the central cavity as in a conventional mill, and part circulates through the spiral duct.

The mill with the spiral grooved rolls is provided with thermocouples fastened to the inner shell of each roll. The leads are brought to the end of the roll in a small spiral groove on the outside of the inner shell, then pass to the center of the mandrel and connect to slip rings at one end of the mandrel. An automatic temperature controller-recorder and pneumatically operated valves for each roll are provided to control its temperature.

The rate of heat transfer between the circulating fluid and the surface of these rolls is greatly increased over that of single cavity rolls with a one-inch wall. The temperature-control system on this mill operates satisfactorily for mixing compounds that require only small amounts of power, particularly if

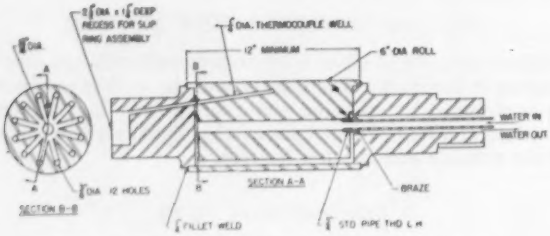


FIG. 5.—Mill roll designed at National Bureau of Standards.

the temperature of mixing is not too low. However, when rubber compounds requiring large amounts of power are mixed at 104 or 122° F, there is a temperature difference as high as 30° F between the thermocouples and the roll surface, and there are temperature differences of as much as 10° F on the roll surface. The respective differences are caused mainly by the interface between inner and outer shells and by the long continuous spiral duct.

NBS ROLLS

Figure 5 shows the design of a roll developed at the National Bureau of Standards, based on experience with rolls previously described. In this roll the circulating fluid enters the central cavity and returns through 12 parallel ducts $\frac{3}{8}$ inch in diameter, with center lines $\frac{5}{8}$ inch from the surface. A well is provided to permit a thermocouple being placed within $\frac{1}{4}$ inch of the roll surface. The thermocouple lead wires are connected to slip rings at the end of the roll shaft.

HEAT TRANSFER CHARACTERISTICS

The relative heat transfer characteristics of the four rolls investigated were determined by circulating water at approximately 70° F through the rolls until steady state conditions were reached. The temperature of the circulating

water was then increased by 100° (i.e., to about 170° F), and the temperature of the roll surface was measured at frequent intervals. The rate of water flow was 3.5 to 4 gallons per minute, except in the case of the spiral grooved roll, in which the resistance reduced the flow to about two gallons per minute, even though the pressure was increased five-fold over that used for the NBS roll.

The increase of temperature of each roll surface is shown as a function of time in Figure 6. The time required for the temperature of the surface of the roll with a two-inch wall to increase 50° F was more than five minutes. Reducing the wall thickness of the roll to one inch decreased this time to 2¼ minutes. For the spiral grooved roll, this time was 1.2 minutes, and for the NBS roll it

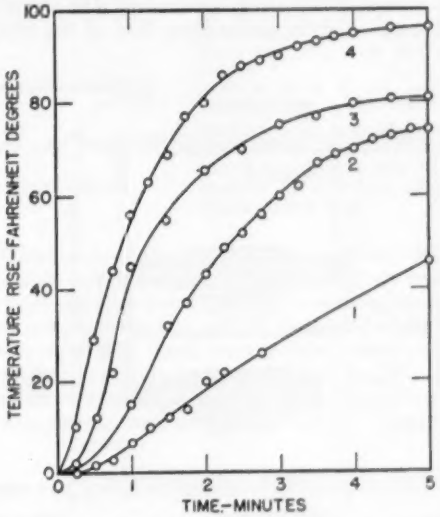


FIG. 6.—Temperature changes of mill roll surfaces following an increase of 100° F in the temperature of the circulating fluid: (1) central cavity roll with a wall thickness of two inches; (2) central cavity roll with a wall thickness of one inch; (3) spiral grooved roll, (4) NBS roll.

was about 0.8 minute. It was also noted that the maximum temperature differences on the surface of the NBS roll was 2° F.

TEMPERATURE CONTROL DURING MIXING—NBS ROLLS

The following systems for controlling the surface temperature of the NBS rolls were investigated:

(1) Automatic recorder-controller and mixing valve for each roll actuated by thermocouples in the outlet water from the rolls.

(2) Same as (1) except actuated by thermocouples in the rolls.

(3) Single automatic recorder-controller and mixing valve actuated by thermocouple in the fast roll (33.6 rpm.).

(4) Same as (3) except actuated by thermocouple in the slow roll (24 rpm.).

In the first system the temperature of the outlet water was held constant, but that of the roll surfaces depended on the power required to mix the com-

pound. For mixing GR-S carbon black compounds, the surface temperature reached more than 10° F above the desired temperature. In order to utilize this system, it would be necessary to adjust the control temperature of the exit water for the particular compound being mixed in order to maintain temperature on the roll surfaces near the desired point.

The other three systems were satisfactory for maintaining the temperature on the roll surfaces close to the control point. The second system provided the best control, since there was independent control of each roll. This system, however, required dual control equipment, and the small improvement in precision hardly justified the additional cost.

The fourth system was adopted for mixing rubber compounds banded on the slow roll. In mixing most rubber compounds with this system, the surface of the fast roll became slightly cooler than that of the slow roll. The only

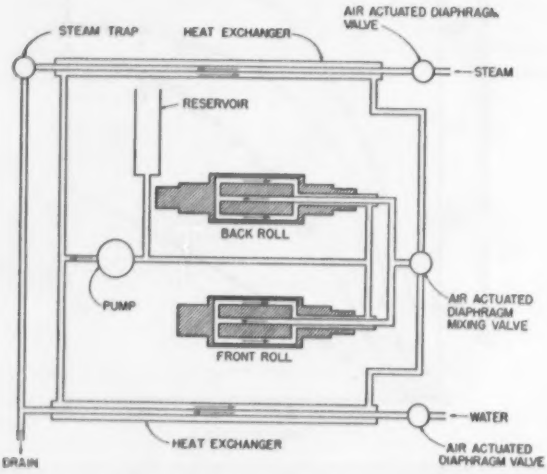


FIG. 7.—Circulating system for heat transfer fluid.

exception thus far noted occurred in mixing butyl rubber compounds, when the fast roll surface became hotter than that of the slow roll.

In mixing rubber compounds banded on the fast roll, the third system was preferable. A switch could be provided to change from one system to the other.

In order to minimize scale formation in the roll which would reduce the rate of heat transfer, the fluid passing through the rolls is circulated in a closed system, as shown in Figure 7. Two heat exchangers are used for heating or cooling, as required.

The controlled air pressure regulates the position of the three air-actuated diaphragm valves. The three-way pneumatically controlled mixing valve operates in a range of air pressures from 5 to 11 lb. per sq. in. (gauge). The pneumatically controlled water valve begins to open as the air pressure decreases below 9, and is completely open at 2 lb. per sq. in. (gauge). The pneumatically controlled steam valve begins to open as the pressure increases above 9 lb. per sq. in. (gauge) and is completely open at 15 lb. per sq. in. (gauge).

For the water a ½ inch V-port valve is used, and for the steam a ¼ inch needle valve. For precise control, positive positioners are required on all valves.

COMPOUNDS AND MIXING PROCEDURES [4]

Elastomer	Formula and mixing procedure
RSS Natural Rubber	Sections 3, 4, 5 (a), and 6 (a) for channel black type
X-761 GR-S (GR-S 1500)	Sections 3, 4, 5, (c), and 8 (a) for GR-S-10 channel black type
X-537 GR-S (GR-S Black Masterbatch containing 55 parts HAF Black phr.)	Sections 3, 4, 5 (c), and 8 (a) for GR-S-10 channel black type except for using 155 parts of the GR-S black masterbatch and omitting the EPC black and step 3 in the mixing procedure
GR-1-18	Sections 3, 4, 5 (e), and 9 (a) for channel black type
Hycar OR-25	Sections 5 (f) and 10 (a) except that 20 minutes, instead of 7, were required to add the black in step 2
Neoprene GN-A	Sections 3, 4, 5 (d), and 7 (a) for channel black type

The surface temperature of the fast roll was measured with a surface pyrometer every 30 seconds during mixing compounds of six rubbers on the NBS rolls, using the temperature control system recommended above. The formulas and mixing procedures described in ASTM Designation D15-52T[4] were used. Compounds containing carbon black were selected, since control of their temperature during mixing, particularly that of GR-S X-537 is the most difficult. The control temperature was 104° F for the butyl (GR-I-18) compound, 158° F for the natural-rubber compound, and 122° F for the others.

EXPERIMENTAL RESULTS

The deviations of the surface temperature of the fast roll from the control temperature were plotted for the entire period of mixing each compound, as shown in Figure 8. The rubber was placed on the rolls at zero time. The surface temperature immediately increased, but was under control within two minutes, except in the case of GR-I-18 and Hycar OR-25. GR-I-18 behaved anomalously, as previously noted. Hycar OR-25 formed a lacy, instead of a solid band, and did not adhere tightly to the slow roll until most of the carbon black was added.

The maximum deviation for any compound was 7° F, and the deviation during the major portion of the mixing period was usually within 2°, except for GR-S X-537 and GR-I-18. The surface temperature of the fast roll was about 3° F lower than the control point during mixing of GR-S X-537 and about 6° F higher during mixing of GR-I-18. In both cases the surface temperature of the slow roll was constant within the precision of the measurements (about 1° F).

If each roll were separately controlled, the surface temperatures of both rolls would be expected to be within 2° F of the control point, except possibly for the first two minutes after the rubber has been banded on the rolls. When the rubber compound was removed from the rolls, there was a temporary decrease of the surface temperature of both rolls. When the compound was

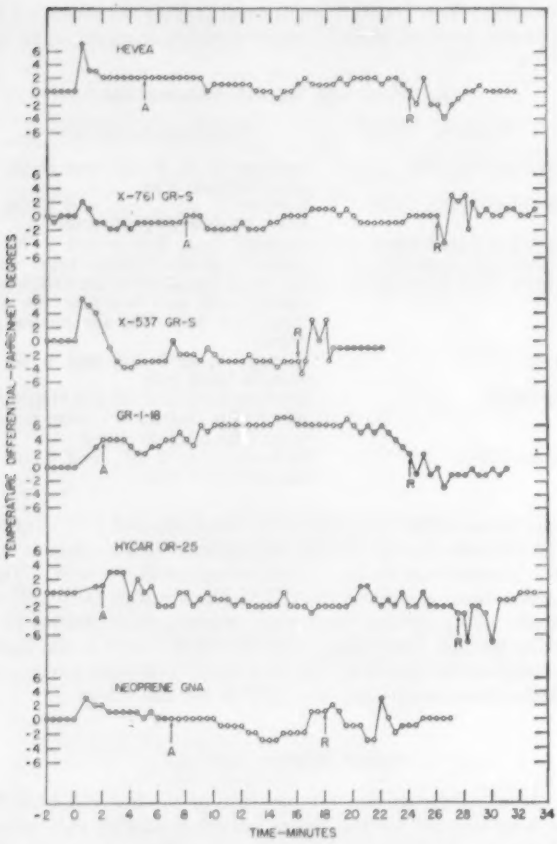


FIG. 8.—Variation of surface temperature of the fast roll during mixing of rubber-black compounds on NBS rolls. The regulating thermocouple was in the slow roll. Rubber was put on the rolls at zero time; addition of black began at A, and the compound was first removed from the rolls at R. The zero points on the temperature differential scales correspond to 158° F for Hevea, 104° F for GR-I-18, and 122° F for other rubbers.

rolled and passed end-wise through the rolls, the surface temperature fluctuated about 4° F above and below the control point.

SUMMARY AND CONCLUSIONS

A study was made of the effect of the surface temperature of the rolls of a 6 × 12-inch laboratory mill on the properties of GR-S compounds and means of controlling this temperature. It was found that the properties of the GR-S compound depend on the surface temperature of the mixing rolls.

No practical method of controlling the temperature of conventional rolls was found because of the slow rate of heat transfer. Therefore three types of special rolls, including one designed at the National Bureau of Standards, were

investigated. The heat transfer characteristics of the NBS rolls permitted automatic control of their temperatures to within 7° F during mixing of natural rubber and several synthetic elastomers, with only one controller being used.

A mill with the special NBS rolls has been in operation for about a year, and has resulted in a marked improvement in the control of mixing of rubber compounds. The automatic temperature control has been much more convenient than manual control, and has saved considerable time, since the rolls do not have to be warmed by milling scrap rubber.

REFERENCES

[1] Report of the Physical Testing Committee of the Division of Rubber Chemistry, *Ind. Eng. Chem.* **17**, 535 (1925).

[2] Schade and Roth, "Developments and Improvements in Methods of Stress-Strain Testing of Rubber", Symposium on Rubber Testing, ASTM-STP **74**, p. 27, American Society for Testing Materials, Philadelphia, 1947.

[3] Reconstruction Finance Corporation, Office of Synthetic Rubber, "Specifications for Government Synthetic Rubbers", Washington, D. C., Revised Ed., Oct. 1, 1952.

[4] American Society for Testing Materials, "Sample Preparation for Physical Testing of Rubber Products", Book of ASTM Standards, Standard D15-52T, Part 6, p. 1.

A STUDY OF SOME HEAT-SENSITIZING AGENTS FOR HEVEA LATEX *

CLAUDE PARIENTE

FRENCH RUBBER INSTITUTE, PARIS, FRANCE

INTRODUCTION

Processes of manufacture which are based on the use of heat-sensitized latex are steadily becoming of more and more importance, particularly in the manufacture of foam rubber products. In a practical way, the only heat-sensitizing agents employed up to 1940 were sodium fluosilicate[1] and ammonium salts in the presence of zinc oxide[2]. However, certain difficulties have been encountered in the use of these agents, the most serious of which are the necessity of washing the gels and the impossibility of storing the sensitized mixtures. Since the last War, numerous patents have been issued concerning the use of heat-sensitizing agents which are very different from the previous agents, both in their chemical composition and in their mode of action.

It is evident that none of these agents is suitable for general manufacturing use and that it is advisable to adapt the heat-sensitization process to the particular conditions of each industry. At present there is available no comparative and at the same time comprehensive study of the subject. It is for this reason that we have attempted to make a systematic comparison of some heat-sensitizing agents and to show their advantages and disadvantages, with the aim of making it possible to choose the agent best suited to the particular conditions.

Table 1 summarizes the results obtained in this work, the details of which are to be found in a more comprehensive report[3]. In the present work, only the results with triacetin and some nitroparaffins are reported.

It is necessary, before undertaking such a study, to make clear certain points. The ideal heat-sensitizing agent should conform to three specifications:

(1) it should be possible to store the latex at room temperature without any change in its properties;

(2) it should be possible, by raising the temperature, to obtain in a short time (of the order of a few minutes) a gel of uniform structure which fills perfectly the molds in which the mixture is poured;

(3) the agent should not change the viscosity or the mechanical stability of the latex.

Actually, if the viscosity of sensitized latex is greater than 400 centipoises, it cannot be used for molding or casting operations, for then it can not be poured into the molds. In addition, the degassing is unsatisfactory.

The mechanical stability should be altered as little as possible so that the manufacturing operations can be carried on with a minimum risk of coagulation.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 32, No. 2, pages 133–137, February 1955. This work was carried out in connection with technical instruction at the French Rubber Institute, and is the subject of research presented at the final examination. Because the work had to be finished in a specified time, it is not so comprehensive as it might otherwise have been. However, the results seem of enough interest to warrant publication.

This stability is of great importance in the manufacture of sponge rubber by churning latex.

TESTING METHODS AND THE APPARATUS USED

The following characteristics were studied for each of the heat-sensitizing agents.

(1) The conditions of gelation.

(2) Changes of viscosity of the mixture of latex, heat-sensitizing agent, and zinc oxide. The amount of zinc oxide added was 3 per cent of the rubber content; while the heat-sensitizing agents were added in different dosages. The viscosity measurements were made with a Brookfield viscometer.

(3) Changes of the mechanical stability of the mixture of latex and heat-sensitizing agent. The apparatus employed was the French Rubber Institute stabilometer, with r.p.m. of 14,000 and test temperature of 35° C.

TABLE 1

COMPARISON OF THE ACTION OF DIFFERENT HEAT-SENSITIZING AGENTS ON SOME PROPERTIES OF LATEX

Heat-sensitizing agent	Storage of the mixtures	Degassing	Heat sensitivity		Mechanical stability	Property of vulcanizates	Aging
			At 50° C	At 70° C			
Sodium fluosilicate (Dunlop)	−	−	+	+	−	0	−(not washed) +(washed)
Ammonium nitrate (Kaysam)	−	−	+	+	−	0	−(not washed) +(washed)
Ammoniacal zinc acetate	0	+	−	+ after 5 hrs.	0	+	+
Diphenylguanidine	−	−	+	+	−	0	−
Gélitex	+	−	+	+	+	+	+
Trypsin	+	+	+	+	0	+	+
Triacetin	+	+	+	+	+	+	+
Nitromethane	+	+	+	+	+	++	+
Nitropropane	+	+	+	+	+	++	+

Legend: ++ excellent; + good; 0 fair; − bad.

(4) The heat sensitivity of latex-sensitizing agent-zinc oxide mixtures and of latex-sensitizing agent mixtures. This determination was made by a method similar to that described by Lepetit[4].

(5) The physical properties of the vulcanizates. For these measurements, mixtures of the following composition were prepared: latex 166, vulcanizing dispersion 10, and heat-sensitizing agent in its optimum dosage. The vulcanizing dispersion was of the following composition: zinc oxide 300, sulfur 200, zinc diethyldithiocarbamate 100, gum tragacanth 3, sodium *o*-phenylphenate 0.6, dispersing agent (Dispersol-LN) 3, and water 393.4.

The mixtures were cast in sheets 2 mm. thick, were gelled at 70° C, and were vulcanized at 110° C to the optimum state. The tensile tests were made with test-specimens 2 × 2 of the French Rubber Institute type.

TRIACETIN

In the use of organic esters as heat-sensitizing agents for latex, two different processes have been used. The first, described by Chassaing[5], specifies the use of isoamyl acetate. This has certain disadvantages; in particular, the forma-

tion of local coagulated masses at the moment of incorporation of the agent and the necessity of letting the mixture mature for four days before it becomes heat-sensitized.

The second process[6] is based on the use of monoesters, such as methyl formate, propyl formate, ethyl acetate, and butyl acetate, which can be easily incorporated into the mixture, but the effectiveness of which varies greatly with the type of latex.

The heat-sensitizing effect is the result of hydrolysis of the ester by the ammonia in the latex. The effectiveness of any ester is, therefore, related to its rate of hydrolysis. This is the reason for tests being made of glyceryl triacetate (commonly called triacetin), which is soluble in water, which hydrolyzes easily in an ammoniacal medium, and which does not cause any local points of coagulation in latex.

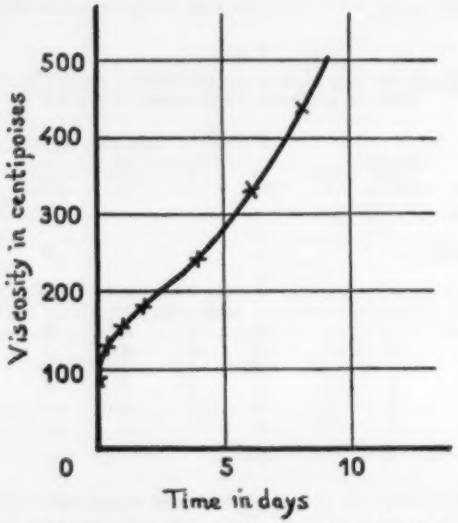


FIG. 1.—Change of viscosity of a latex-triacetin-zinc oxide mixture with time of aging.

Triacetin is capable of heat-sensitizing latex even in the absence of zinc oxide, but the gels obtained are fragile and tear when removed from the mold. With 3 parts of zinc oxide per 166 parts of latex (100 parts of rubber), the heat-sensitizing action is greater, and the gels have excellent properties.

The incorporation of triacetin is very easy; it is sufficient merely to pour it directly into the latex. The optimum dosage is 2 grams of triacetin per 166 grams of 60 per cent latex containing 3 grams of zinc oxide.

Triacetin alone does not change the mechanical stability or the viscosity of latex, even after 45 days' storage of such mixtures. On the contrary, when zinc oxide is present, the viscosity increases considerably, as is evident by the curves of Figures 1 and 2, which record the viscosity values and the times for gelation of a mixture of 166 grams of latex, 2 grams of triacetin, and 10 grams of vulcanizing dispersion.

Figure 3 shows the optimum point on the vulcanization curve. The highest

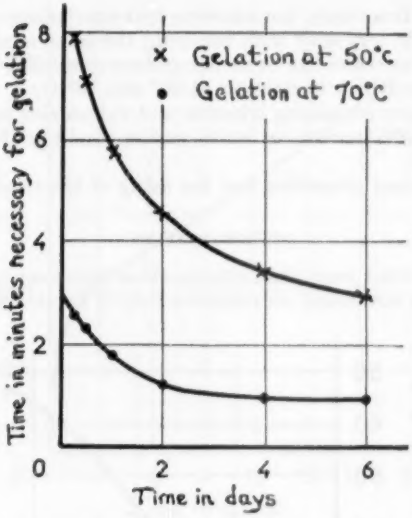


FIG. 2.—Change of time necessary for gelation of a latex-triacetin-zinc oxide mixture with time of aging.

tensile strength reached was 349 kg. per sq. cm. and the maximum tear resistance was 79 kg. per cm.

The curve depicted in Figure 4 shows the results of aging tests in a Geer oven at 70° C.

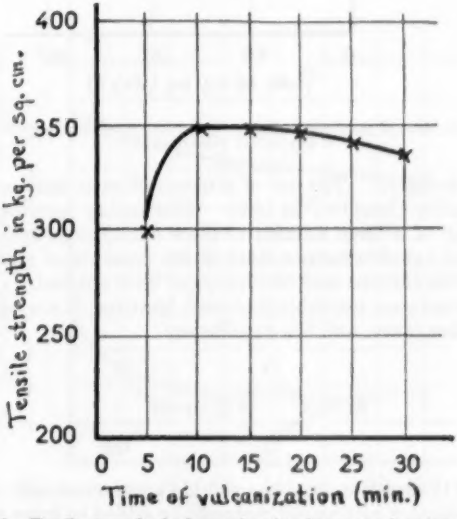


FIG. 3.—Tensile strength of a latex-triacetin mixture as a function of the time of vulcanization.

On the basis of these tests, the following four conclusions can be drawn:

(1) processing is very easy with triacetin; the latex mixtures degas easily and latex-triacetin mixtures can be stored quite successfully;

(2) the heat sensitivity is excellent at 50° and 70° C;

(3) latex mixtures containing triacetin and vulcanizing agents can be kept several days and still remain in quite usable condition for manufacturing operations;

(4) the mechanical properties and the aging of the resulting vulcanizates are good.

NITROPARAFFINS

It is not until recent years that nitroparaffins have been produced industrially, but they have now found an extensive field of application in all branches

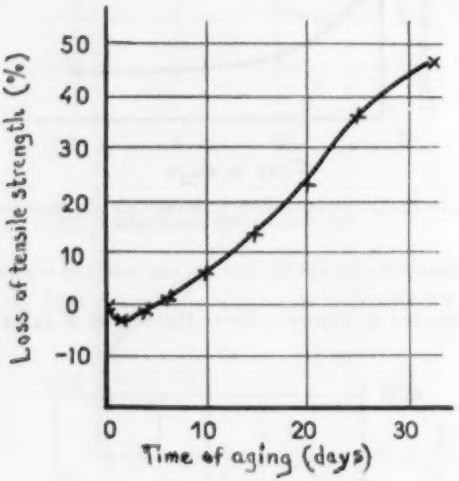
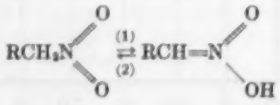


FIG. 4.—Loss of tensile strength of a latex-triacetin mixture as a function of the time of vulcanization.

of the chemical industry. The use of nitroparaffins as heat-sensitizing agents was first reported by Campbell[7] in 1942. This author describes the characteristics and activity of a large number of nitro derivatives, and emphasizes the fact that all these agents sensitize latex in the presence of zinc oxide. In the present work, nitromethane and nitropropane were studied.

These compounds are insoluble in water; however, in ammoniacal medium, solubilization takes place, and the equilibrium:



proceeds in the (1) direction, and the soluble ammonium salt is formed. Because of this reaction, a nitroparaffin should be added to latex slowly and with agitation.

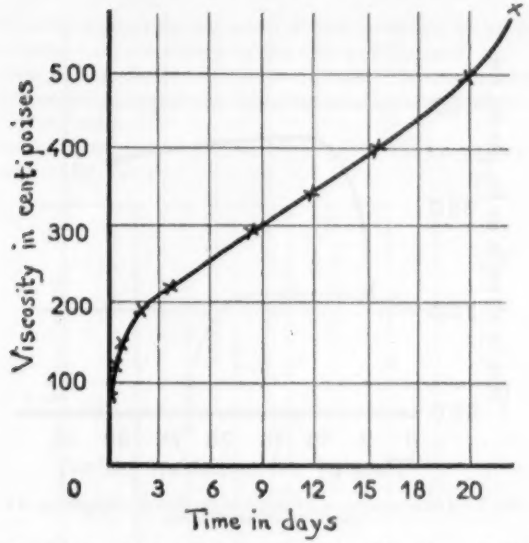


FIG. 5.—Change of viscosity of a latex-nitromethane-zinc oxide mixture with time of aging.

The optimum dosage is 2 grams per 166 grams of 60 per cent latex. Tests have proved that the mechanical stability and the viscosity of latex are not changed when nitroparaffins are added.

Nitromethane.—After 35 days at room temperature, a latex-nitromethane-vulcanizing dispersion did not gel, but assumed the form of a very thick paste.

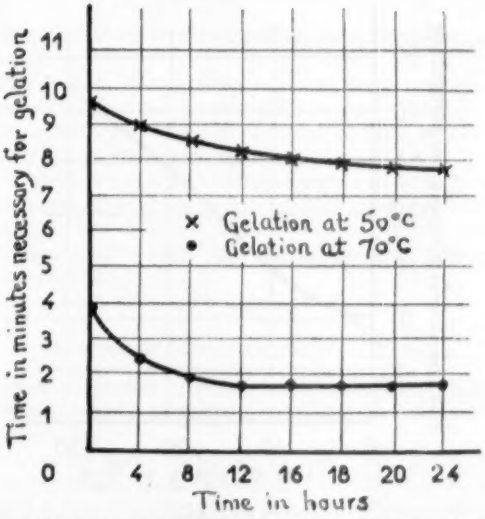


FIG. 6.—Change of time necessary for gelation of a latex-nitromethane-zinc oxide mixture with time of aging.

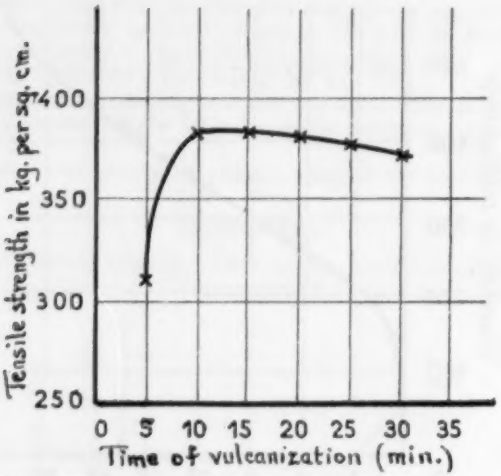


FIG. 7.—Tensile strength as a function of the time of vulcanization of a latex-nitromethane mixture.

The results of viscosity measurements of this mixture and of the times of gelation at 50° C and at 70° C are shown by the curves of Figures 5 and 6.

The latex-nitroparaffin mixture (containing no vulcanizing dispersion) does not change during the course of time except during the first few hours following preparation of the mixture.

The resulting vulcanizates are brown, and the maximum tensile strength

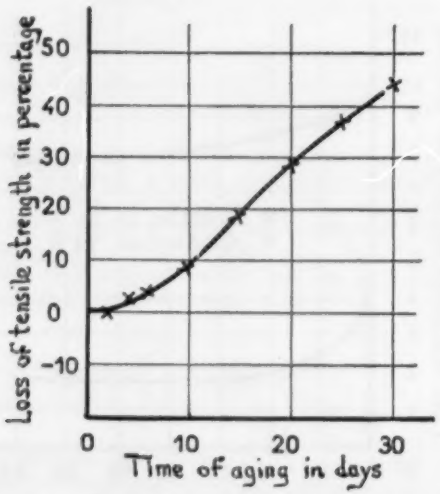
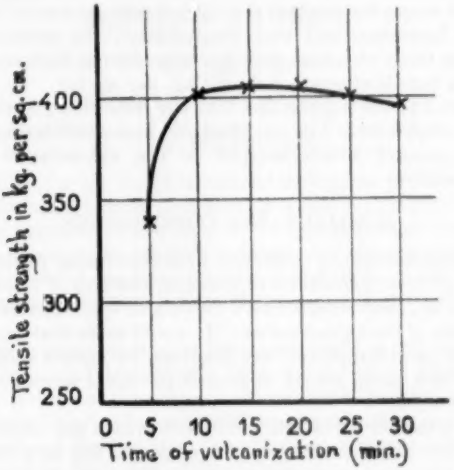


FIG. 8.—Loss of tensile strength of a latex-nitromethane mixture as a function of the time of aging.

(see Figure 7) is 380 kg. per sq. cm. and the tear resistance 88 kg. per cm. The results of the aging tests are shown by the curve of Figure 8.

Nitropropane.—The effect of this nitro derivative is approximately the same as that of nitromethane, except for the mechanical properties and the discoloration of the vulcanizates.

The maximum tensile strength (see Figure 9) is 405 kg. per sq. cm. and the tear resistance 100 kg. per cm.



IG. 9.—Tensile strength of a latex-nitropropane mixture as a function of the time of vulcanization.

With respect to the effects of nitroparaffins, the following conclusions may be drawn:

(1) Processing is easy, the resulting mixtures degas readily, and if they do not contain zinc oxide, they can be stored for several weeks;

(2) The heat sensitivity, which is excellent at both 50° C and at 70° C, appears immediately and changes very little.

(3) Mixtures which contain vulcanizing agents can be kept for several days and still remain in condition suitable for manufacturing operations.

(4) Nitromethane has the disadvantage of giving brown vulcanizates.

(5) The mechanical properties of vulcanizates are remarkably good, especially with nitropropane.

(6) The aging of such mixtures is excellent.

CHANGES OF NITROPARAFFINS IN LATEX

The exceptional properties of vulcanizates containing nitroparaffins have led us to seek an explanation of this characteristic and the mechanism of the reaction of nitroparaffins.

These derivatives are easily reducible; in fact, powdered zinc and water are all that is required to reduce them to oximes, thus : $RCH_2NO_2 \rightarrow RCH{:}\ NOH$.

The latex used in the work described had an oxidation-reduction potential, $Eh = -128$ millivolts, i.e., it was distinctly reducing. Hence, one must take

into account the possibility of reduction of the nitroparaffin in the latex. However, it is impossible, in a medium so complex as latex, to determine, or even to identify in any way, a particular oxime. For this reason it was necessary to make use of an indirect method to confirm this hypothesis.

To this end, propyloxime was first prepared from propylaldehyde. When added to latex in the proportion of 2 grams per 166 grams, this oxime rendered the latex heat-sensitive to the extent that its time of gelation at 70° C was 1 minute and 45 seconds. This time corresponds to that found with nitropropane. This fact seems to confirm the hypothesis; however, when sheets are cast from latex heat-sensitized with propyloxime, the mechanical properties are not so high as those obtained with nitroparaffins as heat-sensitizing agents. For example, the tensile strength was 352 kg. per sq. cm.

These facts lead to the supposition that the reduction reaction is an equilibrium reaction: propyloxime has an effect on heat-sensitization, but it is the unreduced nitroparaffin which imparts to the vulcanizates such excellent mechanical properties.

SUMMARY AND CONCLUSIONS

Latex mixtures containing different heat-sensitizing agents were studied from five points of view: conditions of gelation, changes of viscosity, changes of mechanical stability, heat sensitization (with and without zinc oxide), and the physical properties of the vulcanizates. It would seem that conventional heat-sensitizing agents can be replaced to advantage by agents such as triacetin or nitroparaffins, which more nearly approach the ideal agent as defined at the beginning of this work.

In addition, triacetin gives latex mixtures which are particularly easy to process. As for the nitroparaffins, they are noteworthy for giving vulcanizates with excellent mechanical properties.

REFERENCES

[1] Chapman (to Dunlop Rubber Co.), British patent 332,525 (Mar. 21, 1929).
[2] British patents 391,511 (1933) and 745,321 (1933); U. S. patent 2,014,253 (1935).
[3] Pariente, Claude, "Comparison of Heat-Sensitizing Agents for Latex", unpublished report of the French Rubber Institute, 1952.
[4] Lepetit, Thesis CNAM, Mar. 1947.
[5] Chassaing, French patent 859,335 (May 10, 1939).
[6] Société Auxiliare de l'Institut Français du Caoutchouc, French patent, provisional no., 569,580.
[7] Campbell, *Ind. Eng. Chem.* **34**, 1106 (1942).

INFLUENCE OF SALT COAGULANTS ON THE PROPERTIES AND ON THE AGING OF RUBBER PRODUCTS MADE BY THE DIPPING PROCESS *

A. THORSRUD

FRENCH RUBBER INSTITUTE, PARIS, FRANCE

INTRODUCTION

Among methods for the direct industrial utilization of latex, one of the most widely used is the manufacture of rubber products by coagulant dipping, which involves coating the form with a layer of a coagulating agent and then dipping this in the vulcanizable latex mixture. Because of the coagulant on the surface of the form, a deposit of the latex mixture is obtained, which, after drying and vulcanization, gives a finished article of the same shape as that of the mold employed.

Although few systematic studies have been made in this field, it is generally believed that the coagulating agents have a deleterious effect on subsequent aging. Flint[1] pointed out that the coagulant should be eliminated by washing, and Noble[2] and de Vries[3] called attention to the retarding action of most salts. Finally Kirchhof[4] and Rao[5] studied the effects of different salts on the aging of vulcanizates prepared from dry rubber mixtures.

We thought that it would be interesting to study in a systematic way the influence of salts on the properties during processing and on the characteristics of latex deposits obtained by dipping. Martinon[6] had already commenced such a study of calcium chloride and calcium acetate, and had shown the harmful influence of calcium chloride.

EXPERIMENTAL TECHNIQUE

It was necessary to examine, on the one hand, the effect of the cation, and on the other hand, the effect of the anion of a salt. To study anions alone, they were introduced in the form of soluble ammonium salts. We were particularly interested in anions of strong acids.

The cations were introduced in the form of salts of a strong acid or in the form of an acetate. In choosing these salts, consideration was given to their coagulant power, their solubility in ordinary solvents, and their commercial importance. On this basis, we were led to study especially bivalent cations, such as Ba^{++}, Ca^{++}, and Zn^{++} cations.

Table 1 lists the compounds studied, as well as their solubility. However, in the present paper, we shall limit ourselves, in general, to the study of chlorides and nitrates, which are by far the most interesting.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 31, No. 12, pages 977–982, December 1954. This work was carried out in connection with technical instruction at the French Rubber Institute and as the subject of a research project presented at the final examination. Because the work had to be finished within a specified time, it does not pretend to be complete. The results seem, however, to hold enough interest to make them of value in published form.

Composition of the latex mixture.—The recipe of the latex mixture adopted was the following:

Rubber (as 60% latex)	100
Sulfur	2
Zinc ethylphenyldithiocarbamate	1
Zinc oxide	3

The sulfur, accelerator, and zinc oxide were added in the form of a 50 per cent aqueous dispersion.

Testing methods.—For test-specimens, rings prepared by the method of Pirot were chosen. The ammonium salts possess no coagulant power, so it was

TABLE 1

Cation	Anion	Solubility in water*	Solubility in alcohol
NH_4^+	Bromide	59.8 (0)	
	Chloride	29.7 (0)	
	Nitrate	118.3 (0)	
	Sulfate	70.6 (0)	
	Acetate	148 (4)	
	Formate	102 (0)	
	Salicylate	111 (25)	
	Benzoate	19.6 (14.5)	
Ba^{++}	Chloride	3 (0)	Insoluble
	Nitrate	8.7 (0)	Insoluble
	Acetate	76.4 (26)	Slightly soluble
Ca^{++}	Bromide	125 (0)	Soluble
	Chloride	97.7 (0)	Soluble
	Nitrate	102 (0)	Soluble
	Acetate	37.4 (0)	Slightly soluble
Mg^{++}	Chloride	35.3 (0)	Soluble
Sn^{++}	Chloride	83.9 (0)	Soluble
Zn^{++}	Bromide	447 (0)	Soluble
	Chloride**	432 (25)	Soluble
	Nitrate	184.3 (20)	Soluble
	Sulfate	96.5 (20)	Slightly soluble
	Acetate	30 (20)	Slightly soluble

* Solubilities are given in grams of salt per 100 cc. of water. The values in parentheses indicate the temperature in degrees Centigrade at which the determinations were made[7].
** Zinc chloride partially decomposes in aqueous solution.

possible to add them direct, in aqueous solution, to the compounded latex. Dipping of forms in this mixture gives a deposit of rubber containing the ammonium salt, the concentration of which in relation to the rubber is the same as in the latex mixture. As for the salts of bivalent cations, it was not possible to mix them direct into the latex; instead, they were added by the following technique:

(1) Simple dipping of the form in the latex mixture and drying of the deposit for several seconds, until a film is formed.

(2) Dipping of the form carrying this deposit into the aqueous solution of the coagulant salt and elimination of any excess on the end of the form by means of filter paper.

(3) Immediate dipping of the form in a latex mixture identical with the first latex mixture, but placed in another receptacle.

The test-rings containing the different salts, and also the control rings, were subjected to three aging tests:

(1) Natural aging on a terrace (October 1952 to January 1953).
(2) Aging in a Bierer-Davis bomb (70° C, pressure of 20 kg. per sq. cm.).
(3) Aging in a Geer oven (70° C).

Measurements of the tensile strength were made at regular intervals, and the oxidizability in a Dufraisse manometer was likewise measured.

ACTION OF DIFFERENT SALTS

PROCESSING OF THE MIXTURES

Ammonium salts.—The addition to the latex mixture of ammonium salts brought about in all cases a thickening, the character of which depended on the

TABLE 2

Cation	Anion	Concentration (%)	Thickening effect	Characteristics of the dipped product: Wetting	Characteristics of the dipped product: Film
NH_4	Bromide	0.5–1.0–3.0	Average	Good	Uniform
	Chloride	0.5–1.5–3.0	Average	Good	Uniform
	Nitrate	0.5–1.0–2.0	Great	Good	Fairly uniform
	Sulfate	0.5–1.0–2.0	Great	Fairly good	Fairly uniform
	Acetate	0.5–1.0–2.0	Fairly great	Fairly good	Average
	Formate	0.5–2.0–2.0	Fairly great	Fairly good	Fairly uniform
	Salicylate	0.5–2.0–4.0	Weak	Fairly good	Fairly uniform
	Benzoate	0.5–1.5–3.5	Weak	Good	Uniform
Sample A				Wetting: good Film: uniform	

nature of the anion. In concentrations higher than 3 per cent (based on the rubber), these salts generally induce coagulation, though this is not immediate. They also play an active part in the wetting of the form by the latex mixture and in the uniformity of the product.

Table 2 summarizes the effects obtained with these salts, in different concentrations, on the thickness and characteristics of the dipped product.

Salts of bivalent cations.—These salts were added as has already been indicated. The amounts of the salts present in the rubber were determined, and Table 3 gives the orders of magnitude of these amounts as a function of the concentration of the aqueous solution of the salt. The coagulating power and the characteristics of the dipped products are also recorded.

PROPERTIES OF THE VULCANIZATES

Table 4 shows the effects of the salts on the optimum times of vulcanization and on the maximum tensile strength.

Sample A, containing no salt, was prepared from a latex mixture containing 60 per cent solids, and Sample B from the same mixture, but reduced to 45 per cent solids. This dilution was necessary because the coagulant salts increase

TABLE 3

Cation	Anion	Concentration of aqueous solution (%)	Salt content of samples (%) Order of magnitude	Coagulating power	Characteristics of the dipped products	
					Wetting	Deposit
Ba^{++}	Chloride	10 20 40	1.5 2.5 3.5	Good	Good	Uniform
	Nitrate	4 8	0.75 1.3	Good	Average	Irregular
	Acetate	10 20 40	1.5 2.5 3.5	Excellent	Good	Uniform
Ca^{++}	Bromide	10 20 40	1.5 2.5 3.5	Excellent	Excellent	Uniform
	Chloride	10 20 40	1.5 2.5 3.5	Very good	Excellent	Uniform
	Nitrate	10 20 40				
	Acetate	6 12 24	1.0 1.75 2.75	Excellent	Good	Uniform—rather hard
Mg^{++}	Chloride	6 12 24	1.0 1.75 2.75	Very good	Excellent	Uniform
Sn^{++}	Chloride*	6 12 24	1.0 1.75 2.75	Weak	Good	Uniformly colored
	Bromide	10 20 40	1.5 2.5 3.5	Fairly good	Good	Uniform
	Chloride**	10 20 40	1.5 2.5 3.5	Poor	Good	Fairly uniform
Zn^{++}	Nitrate	10 20 40	1.5 2.5 3.5	Fairly good	Good	Uniform
	Sulfate	10 20 40	1.5 2.5 3.5	Poor	Good	Fairly regular—hard
	Acetate	5 10 20	0.9 1.5 2.5	Fair	Fairly good	Fairly uniform

* Stannous chloride gives the samples a color varying from yellow green with a 6 per cent solution, to deep brown. This color does not appear while adding stannous chloride, either to pure latex or to the vulcanized dispersion (whether ammoniated or not), but only after a certain period after mixing. It is therefore probable that a certain amount of sulfur is transformed into ions in the vulcanisable latex-dispersion mixture, and that the color which is observed is attributable to stannous sulfide.

** Zinc chloride is partially decomposed in aqueous solution.

greatly the thickness of the deposit. Only the results obtained with the chlorides and nitrates are recorded in Table 4; the others are of less interest, and it did not seem worthwhile to include the results. It should be pointed out that, for practical reasons, vulcanization was carried out after storage for two months at ordinary temperature and that the samples had by that time reached their optimum time of vulcanization, but on the other hand had not exceeded it, as was proved experimentally.

TABLE 4

Cation	Anion	Hygroscopicity	Salt content of the sample (%)	Optimum vulcanisation (min. at 110° C)	Tensile strength (maximum kg. per sq. cm.)
Sample A (starting with the 60 per cent mixture)				0*	365
	Chloride	—	0.5	23	360
			1.5	23	310
NH_4^+			3.0	27	270
	Nitrate	—	0.5	27	340
			1.0	27	320
			2.5	27	290
Sample B (starting with the 45 per cent mixture)				0*	343
	Chloride	—	1.5	15	290
			2.5	20	247
Ba^{++}			3.5	32	235
	Nitrate	—	0.75	0*	250
			1.3	0*	240
	Chloride	+	1.5	15	269
			2.5	25	230
Ca^{++}			3.5	32	153
	Nitrate	+	1.5	17	296
			2.5	16	276
			3.5	15	256
	Chloride	+	1.5	36	277
			2.5	40	210
Zn^{++}			3.5	45	136
	Nitrate	+	1.5	17	247
			2.5	28	233
			3.5	42	180

* The zero value signifies that the samples reached their optimum tensile strengths after storage of the ring test-specimen at room temperature for two months.

It was found that, with the exception of barium nitrate, all the salts retard vulcanization so that this does not take place in the cold. The greater the concentration of the salt, the more pronounced is the retardation, except for calcium nitrate, for which the optimum does not seem to vary with the content of nitrate.

Tensile strength decreases and is more pronounced, the greater the content of salt. This decrease is less for ammonium salts than for coagulant salts. From this fact it may be concluded that the cations have a greater effect on vulcanization than do the anions. Since the decrease of tensile strength is

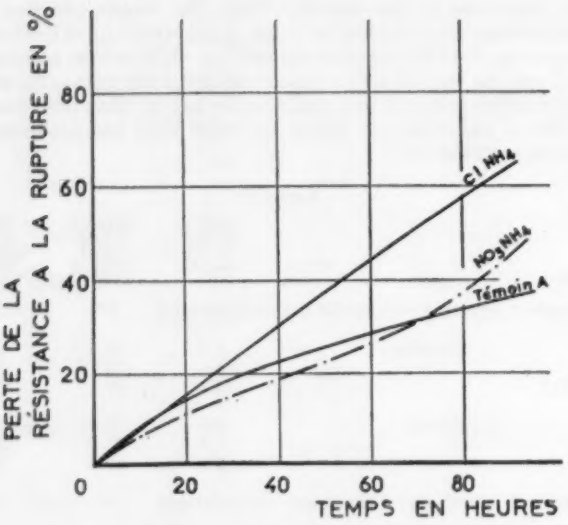


FIG. 1.—Percentage loss of tensile strength as a function of the time of aging in a Bierer-Davis bomb. The abscissa indicates the time in hours; the ordinate the loss of tensile strength. The curve designated as Temoin A is Sample A as described in the text.

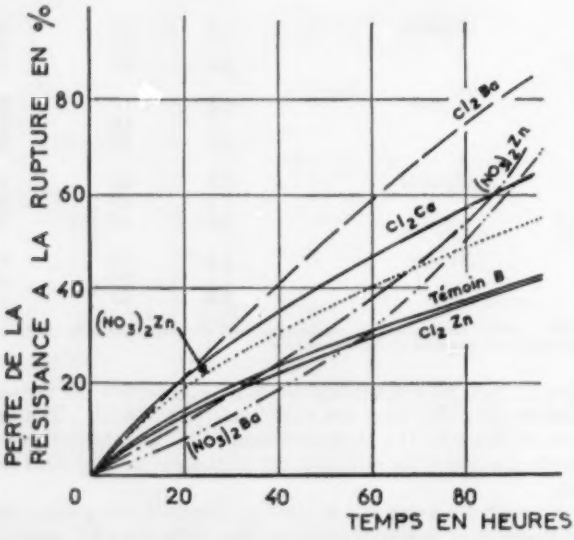


FIG. 2.—Percentage loss of tensile strength as a function of the time of aging in a Bierer-Davis bomb. The abscissa indicates the time in hours; the ordinate the loss of tensile strength. The curve designated as the curve Temoin B is Sample B as described in the text.

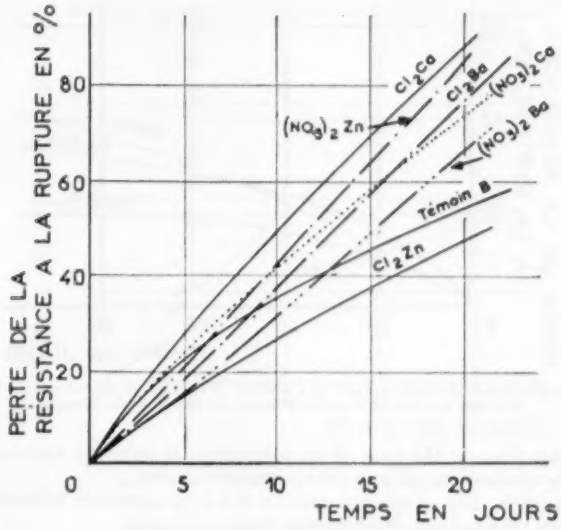


FIG. 3.—Percentage loss of tensile strength as a function of the time of aging in the Geer oven. The abscissa indicates the time in days; the ordinate the loss of tensile strength.

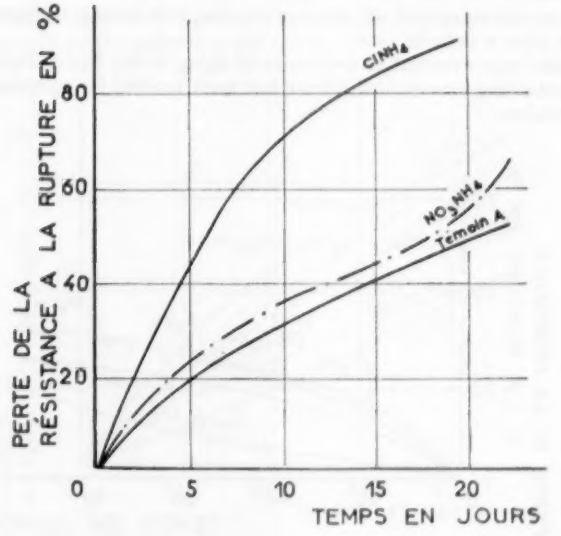


FIG. 4.—Percentage loss of tensile strength as a function of the time of aging in the Geer oven. The abscissa indicates the time in days; the ordinate the loss of tensile strength.

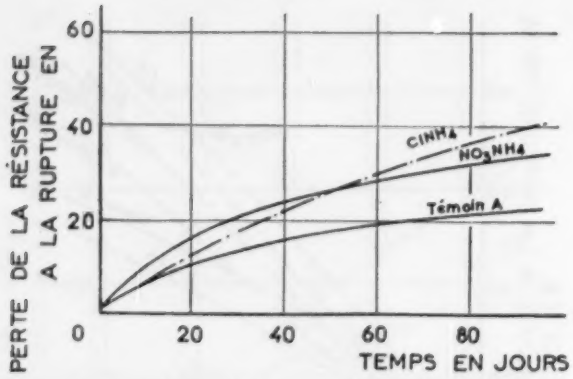


FIG. 5.—Percentage loss of tensile strength as a function of the time of natural aging. The abscissa indicates the time in days; the ordinate the loss of tensile strength.

much greater than in the case of an inert filler, it must be assumed that the ionic nature of the salts plays a rather important role.

With the exception of calcium nitrate, the hygroscopicity of coagulant salts exerts a very pronounced effect on the tensile strength.

AGING AND OXIDIZABILITY

Figures 1–8 show the effect of ammonium salts on aging and on oxidizability.

These results lead to the following conclusions: (1) Nitrates are less harmful to aging than chlorides, and (2) Most of the ring test-specimens become fat-like or resinous after a definite time.

The slight improvement of resistance to aging in the Bierer-Davis bomb of samples containing ammonium nitrate has been verified for mixtures prepared from dry rubber.

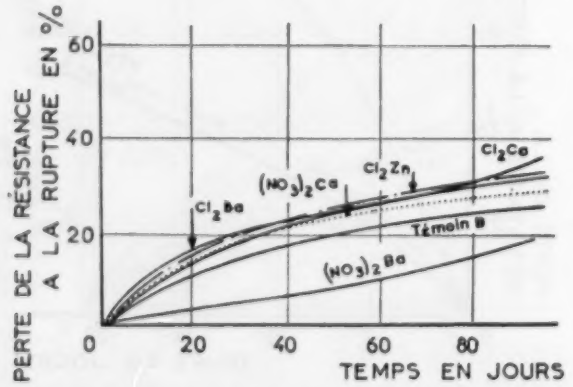


FIG. 6.—Percentage loss of tensile strength as a function of the time of natural aging. The abscissa indicates the time in days; the ordinate the loss of tensile strength.

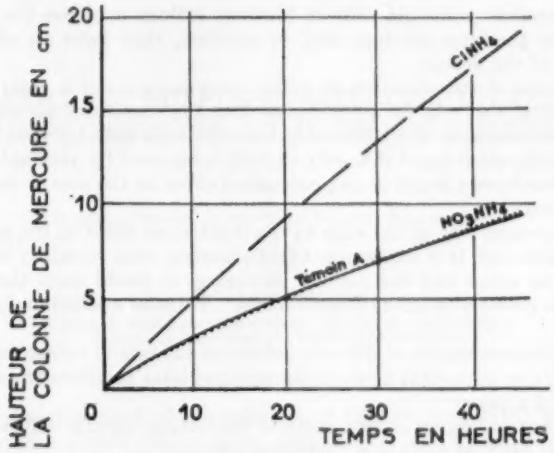


FIG. 7.—Oxidisability in a Dufraisse manometer as a function of time. The abscissa indicates the time in hours; the ordinate the height in mm. of the mercury column. The curve designated as Temoin A is Sample A as described in the text.

CONCLUSIONS

The limited time which we had for this work permitted us to give only an outline of the effects of different salts on processing and on the properties, notably aging, of rubber articles prepared by the dipping process. Nevertheless this work justifies the following conclusions.

1. Ammonium salts have a thickening effect on a latex mixture, the extent of which depends on the nature of the anion.

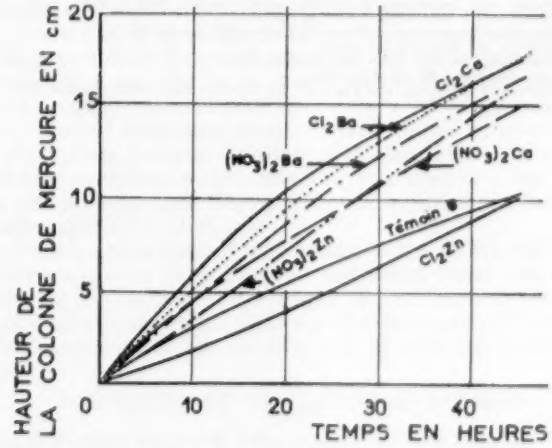


FIG. 8.—Oxidisability in a Dufraisse manometer as a function of time. The abscissa indicates the time in hours; the ordinate the height in mm. of the mercury column. The curve designated as Temoin A is The curve Temoin B is Sample B as described in the text.

2. Ammonium salts and salts of bivalent cations influence the wetting of the form by the latex mixture and, in addition, they have an effect on the uniformity of the deposit.

3. The rate of vulcanization of rubber containing a salt is greatly retarded and, in general, this retardation increases with the content of the salt.

4. Tensile strength is considerably lowered, especially by salts of bivalent cations; on the other hand it is only slightly influenced by ammonium salts.

5. Cations have a much more pronounced effect on the rate of vulcanization than do anions.

6. In a general way all the salts have a deleterious effect on the aging of vulcanizates, although it is impossible to differentiate with certainty between the effects of the anion and the cation. However, it would seem that chlorides have a more deleterious effect than acetates. Nitrates are definitely less harmful.

7. The hygroscopicity of the salts influences the rate of vulcanization, but it does not play so important a role in the aging of latex products as one might be led to expect a priori.

8. The natural aging of test samples containing barium chloride, calcium chloride and calcium acetate is particularly poor.

In addition, the present work confirms the fact that different results are obtained by different methods of aging and seems to make it advisable to replace calcium chloride by calcium nitrate. Nevertheless, the avoidance of inorganic salts of any kind is recommended.

Finally it should be pointed out that the structure of rubber in a product which has been washed (microporous) is not the same as that of rubber which has not been washed, as in the present work; consequently one cannot apply these conclusions to latex products which have not been through the washing process.

REFERENCES

[1] Flint, "The Chemistry and Technology of Rubber Latex", London, **1938**, p. 378.
[2] Noble, "Latex in Industry", New York, **1936**, pp. 158–246.
[3] De Vries, "Report of the Symposium on Rubber", Delft, **1936**, pp. 22–27.
[4] Kirchhof, *Kautschuk* **3**, 239–245, 256–261 (1927).
[5] Rao, Winn, and Shelton, *Ind. Eng. Chem.* **44**, 576–580 (1952).
[6] Martinon, *Rev. gén. caoutchouc* **28**, 109–114 (1951).
[7] Hodgman, "Handbook of Chemistry and Physics", Ed. 32, Cleveland, **1950**, pp. 448–599.

EFFECT OF SULFURIC ACID COAGULATION ON PROPERTIES OF NATURAL RUBBER *

L. L. BEST

RUBBER RESEARCH INSTITUTE OF MALAYA, KUALA LUMPUR

AND

S. H. MORRELL

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, SHAWBURY, SHREWSBURY, SHROPSHIRE, ENGLAND

INTRODUCTION

Earlier investigations[1] of the behavior of rubbers coagulated with sulfuric acid employed a simple rubber-sulfur compound. The results indicated that the rate of vulcanization of such rubbers decreased as the concentration of sulfuric acid used in the coagulation increased, and that a longer period of vulcanization was required to attain a level of technical properties similar to that of rubbers prepared with the more usual coagulants. Although the tests were somewhat restricted, there were no other indications of abnormal properties.

Nevertheless, in 1934, manufacturers expressed considerable alarm at the continued use of sulfuric acid, particularly if they were not warned of the method of preparation before negotiating the purchase of the rubber. Martin and Davey[2] extended the earlier work on sulfuric acid-coagulated rubber to accelerated compounds, and made measurements of tensile strength and elongation at break, before and after aging in a Geer oven for various periods. The results failed to reveal significant differences between rubbers coagulated by sulfuric, acetic, or formic acids. Martin and Davey stated, nevertheless, that manufacturers would be unwilling to employ sulfuric acid-coagulated rubbers without the opportunity of making prolonged and thorough tests. The work reported below illustrates the results of such tests carried out by manufacturers and research establishments on samples of sulfuric acid-coagulated rubber prepared under various conditions, some by estates, some by small holders, and some by the Rubber Research Institute of Malaya. In most cases suitable control rubbers coagulated with formic acid were examined also. The report is divided into sections, each dealing with one aspect of the behavior of the sulfuric acid-coagulated rubber.

Descriptions of the samples of rubber used have been listed in Table 1. In the text they are referred to by a number and letters, which give an indication of the method of preparation. For example, 1S is rubber from the first batch of latex, coagulated with the normal quantity of sulfuric acid; 1SS was coagulated with twice this amount of sulfuric acid, and 1F with the normal amount of formic acid.

PROPERTIES OF UNVULCANIZED RUBBERS

Van der Bie[3], experimenting with mineral acids as coagulants, found that they have no detrimental effect on the raw rubber provided the amount of sul-

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 31, No. 4, pages 133–140, August 1955.

furic acid added is not greater than 5 times the normal dosage. Heinisch[4] claimed that even normal doses of sulfuric acid are likely to give rise to large deformations of the bales under compression and with excessive concentrations suggested the distortion in transite may become serious.

The results suggest that, when normal amounts of sulfuric acid are used, there is very little softening of the rubber. This conclusion was supported by three manufacturers who received samples 3F and 3S, 4F and 4S, 6F and 6S,

TABLE 1

DESCRIPTION OF RUBBERS PREPARED WITH FORMIC OR SULFURIC ACID

Sample	Form	Source of rubber	Coagulant acid	Coagulant concentration (fl. oz./lb. (g./kg.) rubber	Special treatment
1F	Sheets	RRIM,ES*	Formic	1/18 (4.25)	Samples prepared with and without washing during sheeting
1S	Sheets	RRIM,ES	Sulfuric	1/22 (5.25)	
1SS	Sheets	RRIM,ES	Sulfuric	1/11 (10.5)	
1SSS	Sheets	RRIM,ES	Sulfuric	2/11 (21)	
2F	Sheets	Smallholders, Selangor	Formic	Normal practice	—
2S	Sheets	Smallholders, Selangor	Sulfuric	Normal practice	—
3F	Bales	Large European Estate	Formic	1/18 (4.25)	—
3S	Bales	Large European Estate	Sulfuric	1/19 to 1/24 (6.1 to 4.8)	—
4F	Bales	Large European Estate, 1st Div.	Formic	1/18	—
4S	Bales	Large European Estate, 2nd Div.	Sulfuric	1/19 to 1/24 (6.1 to 4.8)	—
5F	Corner Bale samples	Large European Estate	Formic	1/18 (4.25)	—
5S	Corner bale samples	Large European Estate	Sulfuric	1/19 to 1/24 (6.1 to 4.8)	—
6F	Sheets	RRIM,ES	Formic	1/18 (4.25)	—
6S	Sheets	RRIM,ES	Sulfuric	1/22 (5.25)	—
6SSS	Sheets	RRIM,ES	Sulfuric	1/6 (19.3)	—
6SSS+	Sheets	RRIM,ES	Sulfuric	1/6 (19.3)	No washing during sheeting. 0.005% ferric ion on the rubber.
6S+	Sheets	RRIM,ES	Sulfuric	1/22 (5.25)	
7F	Sheet blend	1st lot of smallholders, Meru	Formic	Normal practice	—
7S	Sheet blend	Smallholders, Meru	Sulfuric	Normal practice	—
8F	Sheets	RRIM,ES	Formic	1/18 (4.25)	—
8S	Sheets	RRIM,ES	Sulfuric	1/22 (5.25)	—
8S+	Sheets	RRIM,ES	Sulfuric	1/22 (5.25)	Sulfuric acid by-product of cyclisation process

* Rubber Research Institute of Malaya, Experimental Station.

respectively, and could not distinguish between the pairs of rubbers during mixing and processing. It is only when four times the normal dosage is used that softening becomes significant[5].

SCORCHING DURING PROCESSING

Owing to the existence of different methods of determining scorch time, it is considered advisable to limit the observations in this paragraph to qualitative statements. A manufacturer, using a pure-gum compound accelerated with a

TABLE 2

MOONEY VISCOSITIES OF RAW AND COMPOUNDED RUBBERS

Laboratory	Rubber	V_R*	V_C*
London Advisory Committee for Rubber Research[5]	1F	88	—
	1S	93	—
	1SS	85	—
	1SSSS	78	—
	2F	91	—
	2S	94	—
RRIM[6]	5S	74	33
	5F	77	34
RABRM	6F	84	44
	6S	83	51.5
	6SSSS	73	40.5
	6SSSS+	74	44
	6S+	85	51
	7F	93	54
	7S	89	51
RRIM	8S	80	—
	8S+	80	—
	8F	82	—

* V_R Mooney viscosity of raw rubber measured at 100° C (large rotor, 3 minute value).
** V_C Mooney viscosity under same conditions of ACS.1 compound (rubber 100, zinc oxide 6, stearic acid 0.5, mercaptobenzothiazole 0.5, sulfur 3.5).

mixture of mercaptobenzothiazole and tetramethylthiuram disulfide, noticed that the tendency to scorch of mixes made with rubbers 6F, 6S, and 6SSSS decreased progressively. A second manufacturer, whose compounds were of the tire tread and casing type and were accelerated with *N*-cyclohexylbenzothiazyl-2-sulfenamide, could observe no difference between the rubber 4F and 4S. A third manufacturer, using an unspecified compound, could not distinguish between rubbers, 6F, 6S, and 6SSSS.

RRIM found that, in the ACS.1 formulation, the tendency to scorch was in the order: 1SSSS > 1S > 1F > 1SS, and this was confirmed in a tread mix, using MPC black and mercaptobenzothiazole acceleration, although the differences were much reduced. In a subsequent test, 8S and 8S+ showed less tendency to scorch than 8F when used in the ACS.1 formulation, and also in a commercial compound containing 50 parts of activated whiting and accelerated with benzothiazyl thiobenzoate.

RABRM compared rubbers 6F, 6S, 6SSSS, 6SSSS+, 6S+, 7F and 7S in a tire-tread compound containing 45 parts of HAF black and using *N*-cyclohexyl-

TABLE 3

EFFECT OF STORAGE OF RAW RUBBER IN TROPICAL CLIMATE (RRIM)

Rubber	V_R after storage				
	0 months	3 months	4 months	6 months	9 months
5F	78[9]	84[9]	—	—	—
5S	72	78	—	82	85
8S	80	—	88	—	—
8S+	80	—	88	—	—
8F	82	—	90	—	—

TABLE 4

TENSILE STRESS–STRAIN PROPERTIES

Laboratory	Compound*		Rubber	Cure	TS	EB	Modulus	H	Heat aging (air oven) TSA	Heat aging (air oven) EBA	Heat aging (oxygen bomb) TSA	Heat aging (oxygen bomb) EBA
							M700				2 days (300 psi, 70° C)	
RRIM	ACS. 1		1F	40′/127° C	1810		755	35			129	
			1S		2130		1025	37			117	
			1SS		1790		685	34			126	
			1SSSS		2200		870	37			118	
			2F	60′/127° C	1750		780					
			2S		2105		1220					
							M300				4 days (300 psi, 70° C)	
	MPC	50	1F	30′/127° C	2920		980	70			51	
	MBT	1	1S		2940		995	70			51	
	S	3	1SS		2840		960	68			56	
			1SSSS		3060		1005	71			49	
							M400		7 days at 70° C			
Manufacturer A	ZnO	60	3F	15′/141° C	3500	730	650	45	89	78		
	Antioxidant	0.04										
	MBT	0.73	3S		3420	690	620	44	90	76		
	S	2.81										
									24 hrs. at 100° C			
Manufacturer B	MPC	40	6F	40′/141° C	4050	630		53	90	86		
	Antioxidant	1.75										
	TMT	3	6S		3930	600		57	88	86		
	Te (no S)	0.5	6SSSS		3910	615		54	92	82		
							M300		7 days at 70° C			
Manufacturer C	HAF	18.5	6F	35′/141° C	3885	615	870		87	87		
	RF.1	0.88	6S		3615	610	685		87	86		
	S	2.5										
							M600		14 days at 70° C		4 days (300 psi, 70° C)	
Manufacturer D	ACS. 1		6F	90′/127° C	3200		675		107		70	
			6S		2700		600		112		70	

* Parts by weight, based on rubber, 100. (Zinc oxide and stearic acid used in customary amounts.)

TABLE 4—*continued.*

Laboratory	Compound*		Rubber	Cure	TS	EB	Modulus	H	Heat aging (air oven) TSA	Heat aging (air oven) EBA	Heat aging (oxygen bomb) TSA	Heat aging (oxygen bomb) EBA
							M500		5 days at 70° C			
RABRM	S	5.25	6F	160′/154° C	1780	930	284	16	35	45		
			6S		1840	960	284	34	15	46		
			6SSSS		1570	970	256	32	79	88		
			6SSSS+		1510	940	270	33	91	90		
			6S+		1910	910	327	35	14	43		
			7F		2110	930	327	37	16	47		
			7S		1920	880	356	36	10	40		
									10 days at 70° C		4 days (300 psi, 70° C)	
	CBS	0.4	6F	30′/141° C	2530	680	770	45	95	88	14	52
	S	3	6S		2520	690	780	44	91	88	13	54
			6SSSS		2630	700	810	45	86	89	Failed	
			6SSSS+		2730	710	770	43	90	87	Failed	
			6S+		2060	700	670	43	116	90	Failed	
			7F		2520	710	725	43	92	87	18	59
			7S		2390	710	670	41	100	87	17	56
							M300		14 days at 70° C			
	HAF	45	6F	30′/141° C	3580	490	2010	69	49	49		
	CBS	0.6	6S		3470	480	1860	69	50	46		
	S	2.5	6SSSS		3290	420	2290	71	60	62		
			6SSSS+		3310	420	2200	72	72	62		
			6S+		3630	470	2090	70	59	58		
			7F		3330	480	2040	70	62.5	54		
			7S		3340	460	2100	70	62	54		
							M500		10 days at 70° C*		2 days (300 psi, 70° C)	
RRIM	Activated whiting	50	8S+	25′/140° C	1210	580	940	43	117	95	119	96
	Ureka-C	1.25	8S		1270	580	920	44	112	96	102	93
	S	2.0	8F		1210	560	980	43	112	96	117	98

* Shelf aging for 3 months at 30° C gave comparable figures.
† Parts by weight, based on rubber, 100. (Zinc oxide and stearic acid used in customary amounts.)

TS—Tensile strength (lb./sq. in.).
EB—Elongation at break (%).
M —Modulus (lb./sq. in.) at stated elongation.
H —Hardness, BS°.

TSA —% retention of tensile strength after aging.
EBA —% retention of elongation after aging.
MBT—Accelerator, mercaptobenzothiazole.
TMT—Accelerator, tetramethylthiuram disulfide.
RF.1 —Accelerator, Santocure R.F.1.

CBS —Accelerator, cyclohexylbenzothiazyl sulfenamide.
MPC—Carbon black.
HAF—Carbon black.

benzothiazyl-2-sulfenamide as accelerator: they were unable to find any significant differences in the scorch times.

RATE OF VULCANIZATION AND TENSILE STRESS–STRAIN PROPERTIES

The different rubbers have been evaluated in a variety of compounds by manufacturers and research institutes. There was little quantitative evidence to suggest any difference in the rate of cure between the samples coagulated with formic acid and those coagulated with normal amounts of sulfuric acid. Where excess sulfuric acid had been used to coagulate the rubber, evidence was obtained of retardation of cure in a simple rubber/sulfur mix, but not in accelerated compounds. Table 4 shows the tensile stress-strain properties of various compounds which were given the optimum cure: this being defined as a mean of the optimum times for tensile strength, modulus, and hardness, weighted in favor of the former value.

It will be seen from Table 4 that there is little difference in level of properties between the rubbers coagulated by various methods, and such differences as may exist with unaccelerated compounds disappear entirely when accelerators are used.

AGING OF VULCANIZATES

The results of oven and oxygen bomb tests also are given in Table 4. The four manufacturers of press-cured goods, who submitted quantitative evidence, were not able to distinguish between the methods of coagulation. A manufacturer of vapor-cured surgical gloves compared rubber 5F and 5S. He found in one case that the Geer-oven life of articles made from 5F rubber was 630 hours; that of articles made from 5S, 430 hours. Another experiment by the same manufacturer, using rubbers 6F and 6S, suggested that there was no difference between them. A comparison of rubbers 5F and 5S in loaded compounds, vapor-cured with sulfur chloride, failed to show any difference.

Neither did the results obtained by the research institutes show any difference between the two methods of coagulation in pure-gum and in loaded compounds, with the possible exception of the aging of a pure-gum compound accelerated with *N*-cyclohexylbenzothiazyl-2-sulfenamide in the oxygen bomb. Here, rubbers 6F and 6S could not be distinguished, but those containing excess sulfuric acid or ferric chloride were reduced to stickiness.

FLEXING TESTS

Four manufacturers and one of the research institutes carried out tests to determine resistance to flex-cracking. Since all used different compounds and expressed their results in different ways, a quantitative survey is difficult.

One manufacturer tested vulcanizates of a tetramethylthiuram disulfide compound loaded with MPC black and an accelerated pure-gum compound on the de Mattia machine. There did not seem to be any difference between rubbers 6F and 6S, but rubber 6SSSS was markedly inferior to the other two.

A second manufacturer, using a compound loaded with HAF black and accelerated with Santocure R.F.1, obtained results in the de Mattia test which suggested that 6S was superior to 6F.

A third manufacturer, using a commercial compound of unspecified composition, applied a rotatory motion to one end of a test-piece under compression and measured the time taken to failure. The vulcanizate containing rubber

6S lasted 94 per cent of the time required for rubber 6F, but the significance of this result is not known.

A fourth manufacturer, using an unspecified compound, could find no difference between vulcanizates containing rubber 6F and 6S subjected to the de Mattia test: a vulcanizate containing 6SSSS was markedly inferior. After specimens had been aged for 24 hours at 100° C, vulcanizates containing rubbers 6S and 6SSSS were inferior to one containing rubber 6F.

RABRM, using a tire-tread compound loaded with HAF black and accelerated with *N*-cyclohexylbenzothiazyl-2-sulfenamide, could not differentiate between the rubbers 6F, 6S, 6SSSS, 6SSSS+, 6S+, 7F, and 7S in the de Mattia Test, nor in a heat build-up test, employing the Goodrich flexometer.

MISCELLANEOUS TESTS

PRIM measured the resilience of an ACS.1 vulcanizate containing rubbers 1F, 1S, 1SS, and 1SSSS: no differences could be detected, even after aging for 4 days in an oxygen bomb. Similar experiments on tire-tread vulcanizates loaded with MPC black and accelerated with mercaptobenzothiazole confirmed these results.

RABRM similarly was unable to distinguish between the resilience of rubbers 6F, 6S, 6SSSS, 6SSSS+, 6S+, 7F, and 7S when compounded in a tire tread compound loaded with HAF black and accelerated with *N*-cyclohexylbenzothiazyl-2-sulfenamide. The abrasion losses of these compounds when tested in the Akron machine also were comparable. The tire-tread vulcanizates may have shown a slight diminution of tear strength where sulfuric acid was used as coagulant, but the significance of the results was doubtful.

CONCLUSIONS

The data indicate that the use of sulfuric acid in normal amounts as a coagulant has no deleterious effect on the properties of the raw rubber or on vulcanizates made from the raw rubber. When four times the normal dosage of sulfuric acid was employed, there was a slight softening of the raw rubber, but all samples examined had properties within the normal range of plasticity associated with natural rubber.

The tendency to scorch and the rate of vulcanization of rubbers do not appear to be affected appreciably by the method of coagulation: any differences which may exist are not of such a magnitude as to cause the production of abnormal rubbers.

It would seem that the use of excessive quantities of sulfuric acid during the coagulation of latex may cause some deterioration to the rubber. The sole advantage in using excess would appear to be a reduction of the time needed to complete coagulation. It should be noted, however, that the main reason for the use of sulfuric acid is economic, and it does not seem logical that the producer would use more than is necessary and thereby increase his coagulation costs. If the producer were to use four times the normal dosage of sulfuric acid, the material costs would be about twice those for the normal quantity of formic acid.

ACKNOWLEDGMENTS

This paper has been prepared under the joint aegis of the London Advisory Committee for Rubber Research in Ceylon and Malaya (LAC), the Rubber

Research Institute of Malaya (RRIM), and the Research Association of British Rubber Manufacturers (RABRM), to whom acknowledgment is due for permission to publish. These research organizations wish to acknowledge the willing help given by British and American manufacturers in providing test results and other valuable data.

REFERENCES

[1] *Bull. Rubber Growers' Assocn.* **2**, 343 (1920); **5**, 247 (1923); **8**, 404 (1926); Eaton, *Agr. Bull.*, Federated Malay States, 1918, p. 223; de Vries, *Arch. Rubbercultuur*, **4**, 163 (1920); Wiltshire, *J. Rubber Research Inst. Malaya* **4**, 94 (1932).
[2] Martin and Davey, *J. Rubber Research Inst. Malaya* **5**, 282 (1933).
[3] Van der Bie, *India-Rubber J.* 111, 629 (1946).
[4] Heinisch, *Arch. Rubbercultuur*, 29, 93 (1952).
[5] Baker and Philpott, *J. Rubber Research Inst. Malaya* **12**, 265 (1949).

THE ACCELERATED COAGULATION OF LATEX *

G. E. Van Gils and W. L. Resing

Indonesian Rubber Research Institute, Bogor, Java

INTRODUCTION

The object of the study described in this paper has been a very practical one. However, the results from a practical point of view are rather disappointing, mainly because of economic reasons, but we think them interesting enough to have them published, because some light may be thrown on our basic knowledge of the coagulation phenomena of Hevea latex.

THE COAGULATION OF LATEX

The use of formic acid as a coagulant for rubber latex has been generally accepted, and although several attempts have been made to replace this acid by cheaper or more efficient coagulating agents, it has not yet lost its predominant position. Apart from its technical value, the price and availability of this coagulant in rubber producing areas are decisive factors[1].

The difficulty of obtaining formic acid during the years preceding the last war turned our researches to the use of soaps and other emulsifiers[2]. The classic experiments of De Vries and Beumée-Nieuwland[3] have already indicated the possibility of accelerating coagulation, or more precisely coalescence (i.e., according to De Vries the formation of one coherent mass), by means of special substances.

Altman[4] showed that one of these coalescing agents as separated by van Harpen, proved to be a very simple salt of a fatty acid.

Newton, Stewart, and Wilson[5], looking for methods to accelerate the acid coagulation of latex with a view to preparing rubber continuously, found soaps, especially coconut oil soap, very effective. So the basic idea of the coagulating action and the coalescence or coagulation-accelerating action of soaps was not new. In 1948, however, we faced the problem anew, in the first place from the standpoint of the estate rubber manufacturer, who wanted to economize on the use of formic acid, at that time an expensive item, and, second, from the standpoint of the native rubber grower, who wanted very quick coagulation so as to be able to use the same coagulation appliances several times without requiring more than the usual amount of acid.

EXPERIMENTAL PART

Let us first consider more closely the well known acid coagulation. The time of coagulation depends on the amount of acid added (Figure 1) as well as on the pH ultimately reached (Figure 2). Even at the isoelectric point at pH 4.2, the coagulation time has a certain value, and addition of more acid has no appreciable effect.

In the soap coagulation, the time of coagulation also depends on the amount of soap added (Figure 3).

* Reprinted from the *Archief voor de Rubbercultuur*, Extra No. 2, October 1953, pages 135–148.

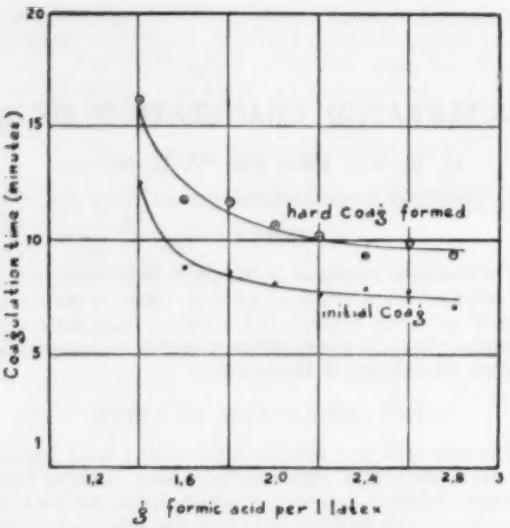


FIG. 1.—Influence of acid concentration on coagulation time.

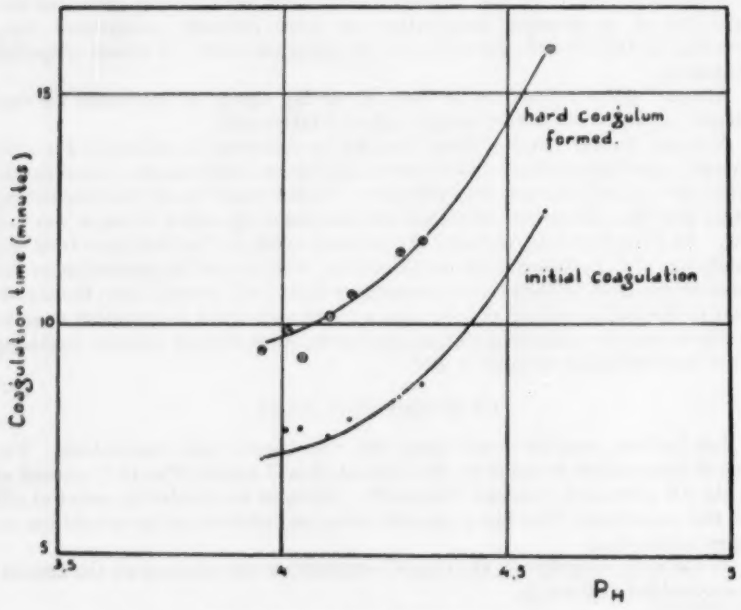


FIG. 2.—Influence of pH on coagulation time.

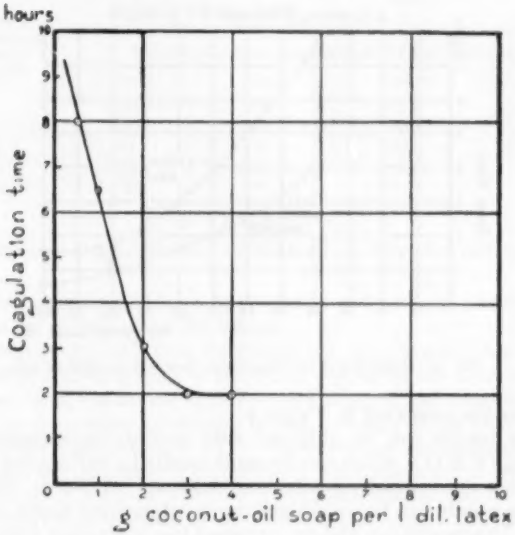


FIG. 3.—Influence of soap concentration on coagulation time.

Other methods for the coagulation of latex are the addition of high value cations, and the addition of surface active cationic soaps. In these cases, however, it is very difficult to obtain a smooth overall coagulation. Moreover, the yellow fraction tends to coagulate separately.

Now we shall consider the following combinations:

(1) Acid + anionic soap
(2) Acid + high value cations
(3) Acid + cationic soaps.

Moreover, a combination of a + b is feasible.

(1) *Acid + anionic soap.*

The effect of soap on the acid coagulation of latex can best be illustrated by the following example.

To two-liter portions of diluted latex (15.9% dry rubber content; total solids 17.2%) are added progressively increasing quantities of formic acid. In a second series acid coconut oil soap is added in addition.

TABLE I

cc. of 1% formic acid	g. formic acid/ kg. rubber	Coagulation time	
		Without soap	With 10 cc. 5% soap
40	1.2	7½ hrs.	4 hrs.
60	1.8	5 hrs.	2½ hrs.
80	2.4	3 hrs.	1¼ hrs.
100	3.0	1¾ hrs.	¾ hrs.
120	3.6	1½ hrs.	½ hrs.

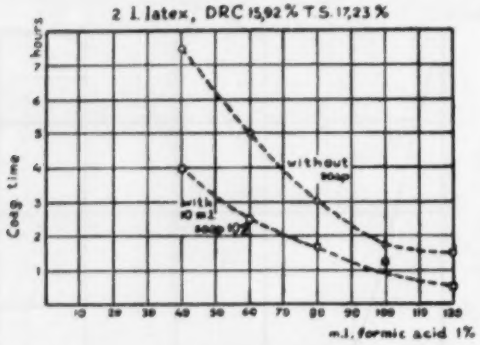


FIG. 4.—Reduction of the coagulation time with coconut oil soap.

The results are presented in Figure 4.

Analogous results can be obtained with another inexpensive soap, viz., Turkey red oil (T.R.O.), which can be made locally by sulfonation of castor oil, as well as with a commercially available sulfon soap (oil 65402) (Figure 5).

The above results can be considered representative for many other types of detergents. The results can also be expressed in a somewhat different manner, namely, by keeping the acid concentration constant and varying the accelerator concentration.

The following experiments were carried out on a technical scale. The latex was diluted to 16 per cent dry rubber content, and coagulation was effected by the addition of 375 cc. 1 per cent formic acid per kg. rubber. Instead of the time after which coagulation sets in, the time after which the coagulum was ready for milling into sheets was observed.

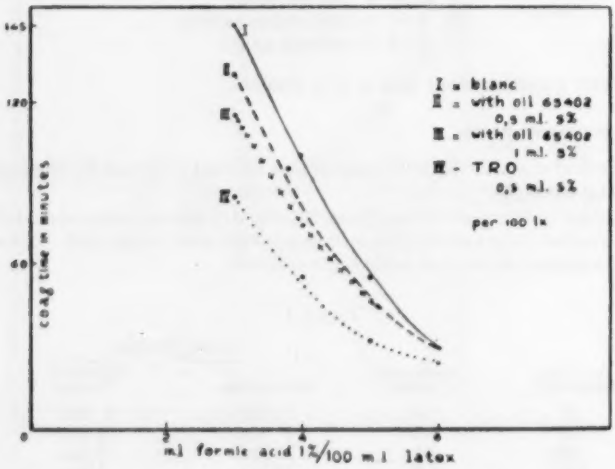

I = blanc
II = with oil 65402 0,5 ml. 5%
III = with oil 65402 1 ml. 5%
IV = T R O 0,5 ml. 5%
per 100 l.x
coag time in minutes
ml formic acid 1%/100 ml latex

FIG. 5.—Reduction of coagulation time by soaps.

TABLE II

Concentration of soap (% of dry rubber)	Time in minutes of coagulation with formic acid plus			
	Sovatex-A	*Teepol*	*Acto-600*	*Coconut oil soap*
0	105	105	105	105
0.1	—	45	70	—
0.2	—	—	60	60
0.3	60	—	—	45
0.5	55	—	—	40

(—: not observed)

(Sovatex-A is an alkylaryl sulfonate; Teepol an alkyl sulfate).

Many other experiments have been carried out with the above surfactants, in the laboratory as well as on the estate.

Our general conclusion is that the results are very variable, depending on the volume of the coagulating tank or trough as well as on the latex itself (day-to-day as well as clonal variations, time between tapping and coagulation, etc.).

Many other detergents have been tested, but only those mentioned can be recommended for practical use. The concentration recommended is 0.1–0.3 per cent on the dry rubber. The difficulty with this kind of coagulation accelerators is that, although the time of initial coagulation can be reduced considerably, the coagulum tends to be rather soft, so that the overall time of preparation of the coagulum for milling appears to be only slightly reduced.

Higher concentrations of soap, especially in conjunction with lower acid concentrations, moreover, produce a white serum and rubber losses may be ob-

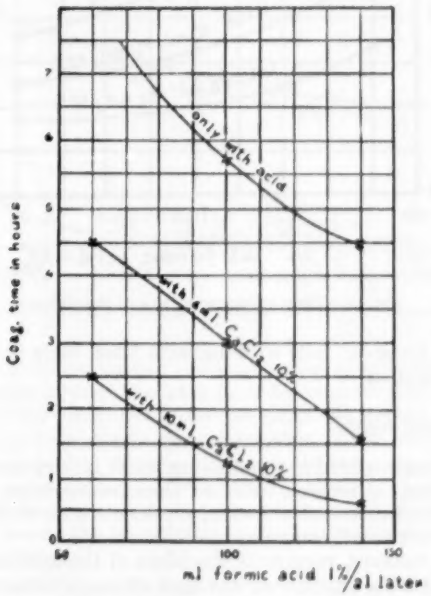


FIG. 6a.—Effect of calcium on acid coagulation.

served. This fact is rather discouraging, because it is with lower acid concentrations that the effect of time-reduction is greatest.

(2) *Acid + highvalent cations.*

High-valent cations, especially calcium or magnesium, when added to the diluting water may sometimes effect a reduction of the coagulation time. Best results have been obtained with salts in which the accompanying anion is monovalent, i.e., calcium chloride. Aluminum salts have proved to be no better than calcium salts. The effect is largest with small amounts of acid.

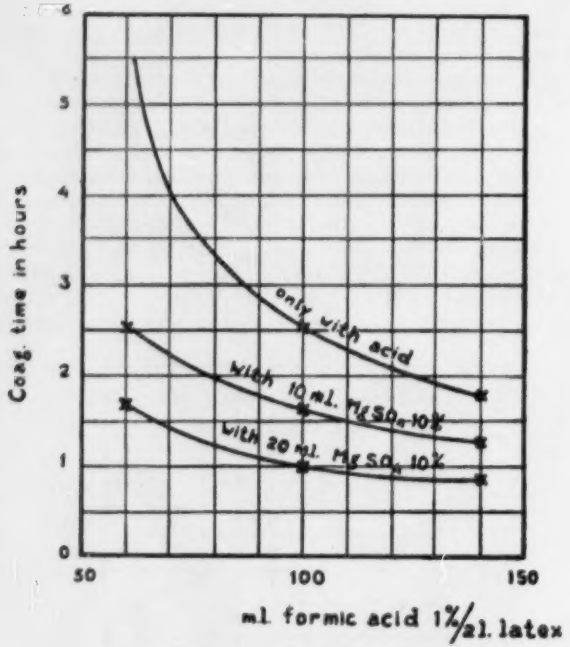


FIG. 6b.—Effect of magnesium on acid coagulation.

This method, however, fails with unstable latex, since the salts added tend to effect precoagulation.

(3) *Acid + cationic soaps.*

These soaps, when added to the diluting water in very small amounts, may have a good effect. However, most of these compounds, containing basic nitrogen, are also effective vulcanization accelerators, so that application must be restricted to very small amounts.

Figure 7, for instance, represents the effect of the addition of Armac-T (a mixture of C_{16} and C_{18} amines) on the time of coagulation as well as on the modulus at 600 per cent stress of a vulcanizate (ACS No. 1 mix).

DISCUSSION

In discussing the described phenomena, we shall begin at the end. Neither the coagulation acceleration with cationic soaps nor that with calcium salts needs an explanation, for it is clear that the negatively charged latex particles are destabilized by the addition of strongly adsorbed positive constituents.

The explanation of the action of anionic soaps, however, is more difficult. Assuming the mechanism of the spontaneous coagulation to be as postulated by the first author, the action of these soaps forming insoluble magnesium salts will need no further explanation. It is recalled that this mechanism is based on the concept that, during the process of spontaneous coagulation, fatty acid

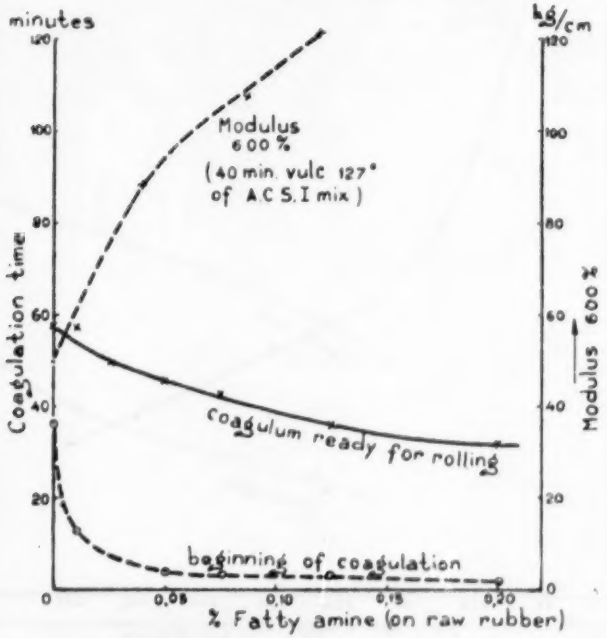


FIG. 7.—Effect of fatty amine on coagulation time and 600 per cent modulus.

soaps are formed by decomposition of lipoid material, and that these soaps adsorbed at the surface layer of the latex particles interact with magnesium ions already present in the latex. It is further emphasized that these lipoids are located in the yellow fraction and that without the yellow fraction no spontaneous coagulation will occur. Neither does spontaneous coagulation take place in the absence of magnesium ions. The displacement in this interface of proteins by soap ions has, moreover, the effect of sensitizing the latex particles towards H^+ ions, due to the insolubility of the fatty acids formed out of these soaps.

Further, attention is drawn to the findings of Newton, Stewart, and Willson[5] that in the series of fatty acid soaps with increasing numbers of C atoms, those

with C_{12} and C_{18} are most active[6]. A similar phenomenon has been found by Bungenberg de Jong[7] in his work on the influence of fatty acid ions on oleate coacervate.

Further it should be remembered that lipases i.e., enzymes, which decompose fatty material, promote spontaneous coagulation.

The action of pancreas lipase is shown in Figure 8.

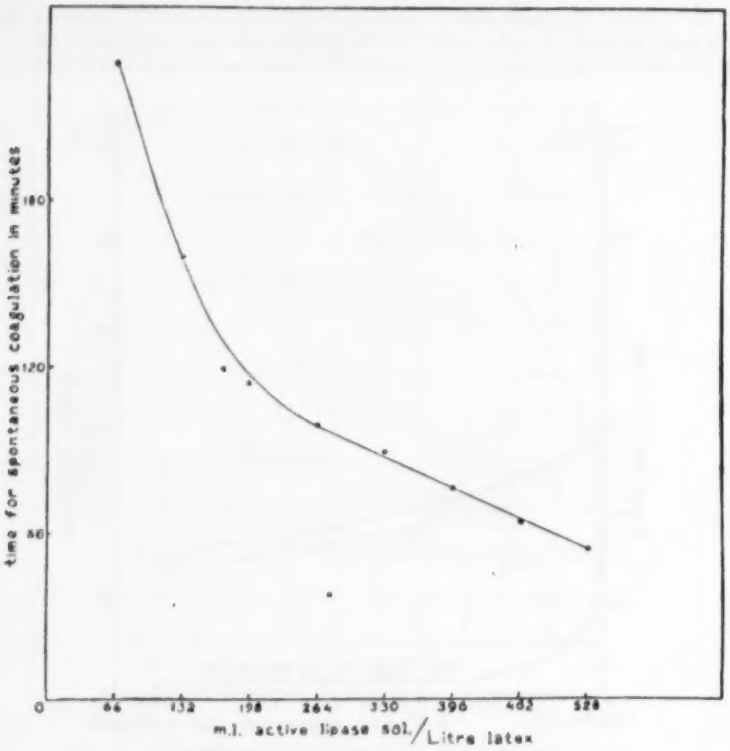


FIG. 8.—Acceleration of spontaneous coagulation by lipase.

Lipase extracted from castorbeans, however, is less active and has an effect only in the presence of acid; in other words, this enzyme may act as a coagulation accelerator.

We shall now stress the following: addition of soap acts in the same sense as the mechanism of spontaneous coagulation. This is illustrated by the fact that the time required for acid coagulation depends on the lapse of time between tapping and coagulation.

The action of soap as an acid coagulant is furthermore dependent on the time elapsed between tapping and coagulation, and the more unstable the latex, the smaller the effect of the acid coagulant. We are even inclined to believe that the process of spontaneous coagulation is not stopped immediately

on addition of the acid. Is not an acid itself incapable of immediately coagulating the latex? And is not a certain period of time required for complete coagulation to take place, during which time spontaneous coagulation occurs, with formation of degradation products? Also, when latex is allowed to stand for some time with ammonia, fatty acid ions are slowly formed, and these replace the proteins in the interface of the particle. The experiment has shown that, on standing with ammonia, the time necessary for the coagulation of the latex

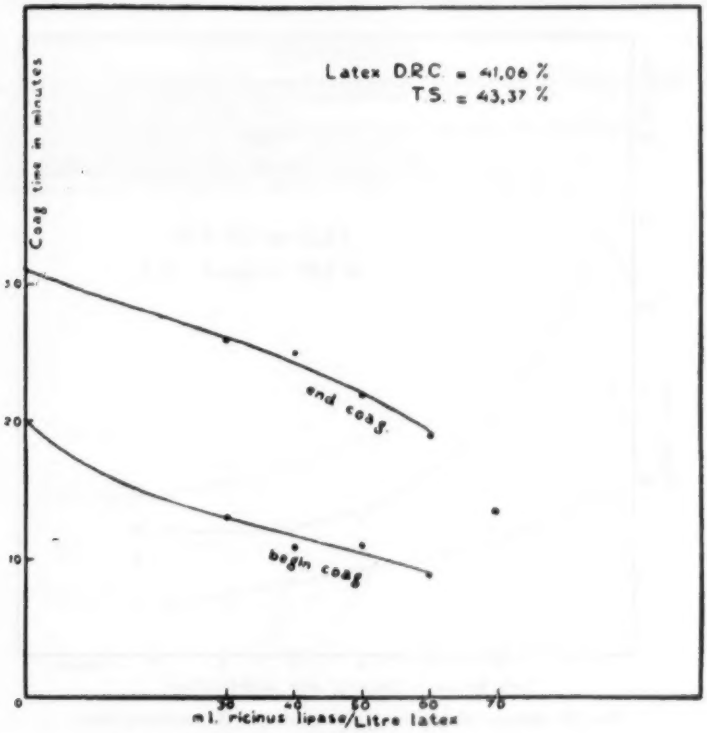


FIG. 9.—Acceleration of spontaneous coagulation by castor lipase.

after acidification is reduced so gradually that, after about one week, the latex coagulates immediately on addition of acid.

Summarizing we may state:

1. Allowing latex to stand for some time, i.e., permitting the processes responsible for spontaneous coagulation to take place, has the same effect as the addition of soap.

2. Acidification in itself, even to the isoelectric point, is not sufficient to coagulate latex immediately. That, after some time, coagulation does take

place must be due to the same processes which are responsible for spontaneous coagulation.

Critics have countered that our theory of the mechanism of spontaneous coagulation is too simple. We agree, for there are facts which cannot be accounted for by this assumption. For example, there is the fact that Teepol, a surface-active agent producing soluble magnesium salts, acts as a coagulant for latex and as a coagulation accelerator.

We are of the opinion that this fact also can be explained when we extend our coagulation theory as follows:

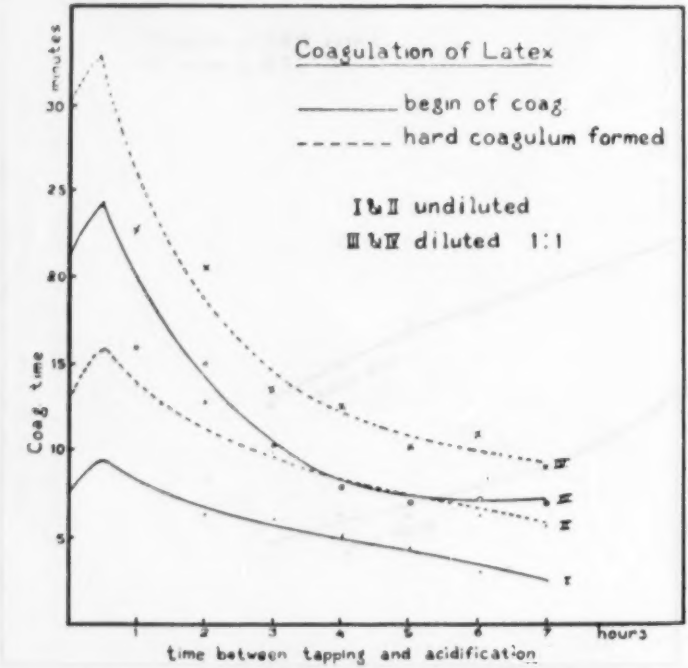


FIG. 10.—Influence of the moment of coagulation on the coagulation time.

According to modern knowledge of emulsions, the structure and the mechanical properties of the monolayers at the surface of the globules are of great importance for the stability. Even if the electrokinetic potential is zero, the rigidity of the interface may prevent coalescence, i.e., fusing together of the droplets. Displacement of the rigid interface skin by a mobile adsorbed monolayer which permits the droplets to coalesce, causes the emulsion to break.

This knowledge will be very useful in explaining the phenomena of the coagulation and coagulation acceleration mentioned. There are well established reasons for assuming that the protein layer around the (virgin) latex globule is rather tough, and prevents the latex particles from coalescing. Even at the isoelectric point (no charge), the latex does not coagulate, i.e., coalesce, immediately.

When, however, soap is added or when spontaneous coagulation is allowed to proceed, this protein interface will be replaced by a soap monolayer, which is much more mobile. Coagulation will then take place if the electrokinetic conditions are such as to enable the particles to get together, i.e., if the concentration of either H^+ ions or Mg^{++} ions is sufficiently high.

Teepol, an ester sulfate, is much less ionized as a sulfonic acid salt. Displacement of the protein layer by Teepol gives a mobile interface which, even at neutral pH, does not carry enough charge to prevent the particles from getting together, and once contact is established, coalescence will proceed.

REFERENCES

[1] It must be borne in mind that industry is steadily progressing. An acid which is a laboratory rarity today may be available in tank wagon loads tomorrow.
[2] Van Gils, *Arch. Rubbercultuur* **25**, 383 (1941).
[3] De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur* **9**, 631 (1925) and other publications.
[4] Altman, *Arch. Rubbercultuur* **24**, 395 (1940).
[5] Newton, Stewart, and Willson, *Ind. Eng. Chem.* **39**, 978 (1947).
[6] Newton, Stewart, and Willson, *Ind. Eng. Chem.* **39**, 978 ff. (Fig. 2) (1947).
[7] Bungenberg de Jong, "Colloid Science", Elsevier Publishing Co., New York, Vol. 2, p. 709.

THE SIGNIFICANCE OF THE YELLOW FRACTION IN SPONTANEOUS COAGULATION *

F. J. PATON

DUNLOP MALAYAN ESTATES, MALACCA, MALAYA

The characteristics of the heavier yellow fraction which is separated on centrifuging fresh latex have been described in the literature. This material is made up of a loose aggregate of particles which have a relatively high specific gravity. It can be dispersed in dilute salt solutions, but tends to coalesce into an irreversible precipitate when diluted with water.

It is still not quite clear what happens when water is added to the yellow fraction. After diluting latex with water, the formation of a layer at the bottom of the tube no longer takes place, the flocculated rubber carrying the bulk of the aggregate to the top of the tube.

The observed phenomena can be explained on the assumption that the yellow fraction is made up of a number of cells, and some evidence for the existence of membranes has been offered by Ruinen. On such an assumption, they can be accounted for as osmotic phenomena. However, this explanation is not entirely satisfactory, since volume shrinkage does not appear to take place in a hypertonic solution.

The concept of van Gils and de Haan's of lutoids presupposes a cellular structure involving rubber particles. Our results have shown that the yellow fraction contains a lipid-protein complex associated with rubber, and it was the object of the experiments described below to determine how far the complex could be freed from rubber. It was found that the stability of the system was too low to permit of a continued washing with salt solution unless the pH was raised somewhat. When first separated, it usually has a pH of 6.2 and is viscous. If the pH is raised, however, to 6.8, it becomes less viscous and is more stable. After washing once or twice by diluting with 0.2 per cent potassium chloride and centrifuging so that much of the rubber is removed, the tendency to flocculate is reduced, and further washing can be carried out at pH 6.0, the pH to which it has a tendency to approach. If the washing is carried out until there is no further appearance of rubber particles in the upper layer, the product still contains a small amount of rubber, but it has not yet been determined whether this is normal rubber and in what way it is associated with the other components. However, a stage has been reached, in some instances, where the bulk of the solids can be accounted for as alcohol-water solubles and proteins. Further data on the nature of the alcohol-water-solubles is given below.

Out experiments so far lead us to suppose that the significant part of the yellow fraction complex is a lipo-protein, possibly a tricomplex involving protein, lipid, and ions. Such complexes are usually supposed to be made up of alternating micellar layers of proteins and lipids bound together by electrostatic forces.

* Reprinted from the *Archief voor de Rubbercultuur*, Extra No. 2, pages 93–102, October 1953.

The most outstanding characteristic of yellow-fraction substances is the sudden fall of pH which occurs on dilution with water, an immediate fall of 0.5 pH resulting from a 20 per cent solution. (A similar but much smaller effect is observed on diluting latex.) Dilution with potassium chloride solution also causes an immediate drop of pH, the effect being somewhat smaller than that of the corresponding volume of water. In both instances the pH falls still further on standing, but this slow fall could be the result of enzyme action; the presence of esterases can be demonstrated.

The behavior of yellow-fraction substances differs somewhat from proteins. Owing to their gegen-ions, proteins react towards salts as if they were acids or alkalis. Below the isoelectric point the pH is raised, for example, by sodium chloride, but at a pH above the isoelectric point it is lowered. It is, therefore, somewhat difficult to understand the behavior of the yellow fraction on dilution, since this ought to decrease the salt concentration and thus increase the pH. However, it is possible to explain the fall of pH on the assumption that flocculation takes place, and in the change from the micellar state, ions are liberated into solution.

The addition of water to the yellow fraction can be seen to cause some flocculation. When an appreciable quantity of rubber is present flocculation is irreversible. Salts however appear to peptize the proteins and give a dispersion. When this is examined under the microscope only rubber particles can be seen and these have Brownian movement. Centrifuging this dispersion in a moderate gravitational field causes the particles to aggregate and collect at the bottom of the tube. Since the specific gravity of proteins is of the order of 1.37 and that of the heaviest lipids not much greater than 1 it must be assumed that the size of the particles in the dispersion is large and that they have a high protein content. Microscopic examination of the separated yellow fraction, after several purifications reveals a fibrous structure, in which a number of rubber particles can be seen to be entrapped. The rubber particles no longer show Brownian movement.

The general behavior of the non-rubber colloids of the yellow fraction seems to be characteristic of lipo-proteins. The thixotropic properties can be attributed to a micellar structure. The viscosity is immediately reduced by adding a small quantity of potassium chloride crystals when the pH falls; finally flocculation takes place. The action of potassium fluoride is similar to that of potassium chloride in that it has a dispersing effect. The pH change is slower than with potassium chloride solution. Potassium fluoride, however, tends to prevent flocculation, since the pH drops, and samples containing it have been kept in a good state of dispersion for 24 hours at pH 5.7. At this pH, potassium chloride dispersions flocculate within an hour.

NATURAL COAGULATION OF RUBBER

It has been demonstrated that when latex is tapped, a septic yellow fraction coagulates on standing and separates from the white fraction, which can then be kept for a long time. This suggests that spontaneous coagulation of latex originates in the yellow fraction.

When first separated, it can be shown that the yellow fraction has a pH lower than the rest of the latex. Latex, in fact can be separated by centrifuging, into 2 layers, the lower of which (Y.F.), has a pH as much as 0.6 lower than the top layer. We have made a study of the natural coagulation of the white fraction vis-a-vis the whole latex. The only difference to be observed was that in the pH range 5.3–5.6, whole latex coagulated after 6 hours, whereas the white

fraction remained uncoagulated. Below pH 5.3, the evidence seemed to show that the white fraction coagulated at least as readily as the whole latex. This high pH zone is probably the important one in spontaneous coagulation. Previous work has shown that latex coagulates naturally at a pH 5.5–6.2, i.e., considerably above the ioselectric point (4.5). The fact that formaldehyde and other substances affecting the properties of proteins prevent coagulation, whereas ordinary antiseptics do not, has established the probability that spontaneous coagulation is the result of enzyme activity. We have shown recently that latex treated with potassium fluoride can be kept in a liquid condition for a considerable time in the pH zone between 5 and 6. With potassium fluoride-treated yellow fraction, the usual fall of pH occurs, but whereas flocculation is apparent, coagulation does not take place if bacterial activity is absent. This suggests that coagulation depends on enzyme activity involving the alteration of the protective layer round the particles (de Vries, coalase?), in addition to the acid forming process.

The suggestion that coagulation is initiated by the interaction of fatty acids with magnesium appears to be an oversimplification. Experiments designed to test this hypothesis give contradictory results from day to day. The susceptibility to detergents also varies, and although fresh latex can usually be coagulated by small additions of substances such as Teepol, this is not invariably the case. The interesting point is that latex is more readily coagulated by small quantities of Teepol, of which the magnesium salt is soluble, than it is by fatty acids, which give insoluble salts. We have recently established that the white fraction is very much less susceptible than whole latex to the action of Teepol. Since detergents are known to precipitate lipo-proteins, it seems reasonable to suppose that this difference of behavior can be accounted for by at least a part of the lipo-protein having been removed in the yellow fraction. There is no reason, however, to suppose there is any sharp qualitative dividing line between the yellow and white fractions. The quantity of yellow fraction separated depends, to some extent, on the conditions under which the latex is centrifuged, and it is necessary to assume that the particles separated correspond to van Gils and de Haan's lutoids. They must be large ones in order to account for the relatively simple method of separation.

There is no evidence that the alcohol-soluble and ether-soluble substances of the yellow fraction are not present also in the white fraction. White fraction latex when ammoniated does not differ greatly from ammoniated whole latex, and this is to be expected, since only about one-sixth of the total alcohol-soluble and ether-soluble substances is separated with the yellow fraction.

The difference between the white fraction and whole latex may be accounted for on the assumption that the latter contains organized lipo-protein complexes, in addition to their component substances. The complexes separate in the yellow fraction and the properties of the white fraction are thus modified. The viscosity, for example, is reduced.

Possibly there exists in latex a large number of lipin or lipo-protein particles of very small size. Such small particles have been established in other biological fluids, e.g., blood serum, where they are less than 0.5 μ in diameter. The characteristics of the yellow fraction are, however, determined by the properties of the large lipo-protein particles, which, when brought together, tend to set up an organized structure.

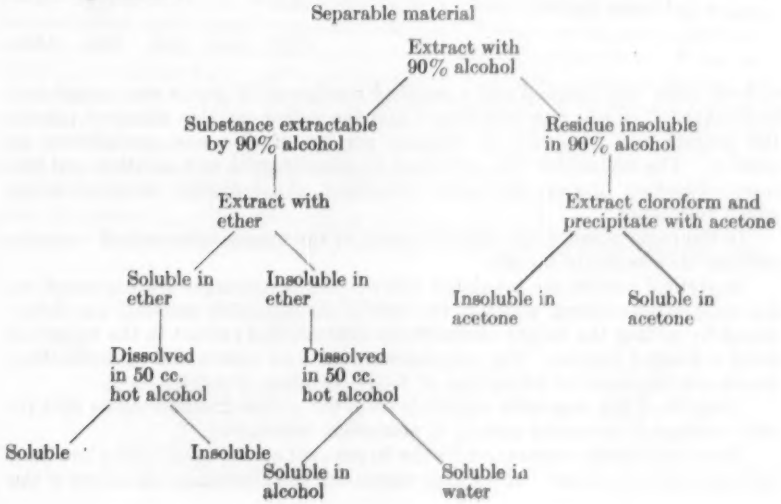
Following de Vries' work, Belgrave suggested that the substance responsible for the coalescence of latex particles was a lipo-protein complex, and evidence would appear to support this suggestion. It is possible to formulate a theory

that spontaneous coagulation is initiated in the lipo-protein micelles, where there are active enzymes which affect the physical properties of the protective proteins, possibly by a process of denaturation. The rubber particles are thus caused to aggregate. In instances where spontaneous coagulation takes place very early and at a high pH, it may be that the physical condition of these lipo-proteins is the determining factor. In stable latexes which persist for a long time (until the pH approaches 5), it can be assumed that the lipins or lipo-proteins exist largely as small particles as in white-fraction latex. Since the lipo-protein complex is so much influenced by salts in the serum, one might expect the mineral content to have considerable importance in determining the initial stability of latex.

EXPERIMENTAL PROCEDURE

The investigation of the chemical nature of the separable non-rubber components of the yellow fraction was based on the usual technique for determination of lipin, protein, water-solubles, etc.

About 100 grams of yellow fraction from 600 grams of whole latex was raised to pH 6.8 with a little ammonia, diluted to 400 cc. with 2 per cent potassium chloride solution and after standing, was centrifuged to yield a top layer containing rubber and a lower viscous yellow layer which was separated, while the upper layer was rejected. The process was repeated until it became apparent that no further removal of rubber was occurring. At this stage the system had a gelatinous appearance resembling precipitated aluminum hydroxide. For clarity, this will be referred to as "separable material". It was washed on a filter paper to remove the added salt and finally placed in twice its volume of 90 per cent alcohol and stirred. The mixture was refluxed for a few hours and then reduced almost to dryness. The solids were filtered on a weighed filter paper and dried. A small amount of filtrate was recovered, and this was made up to about 70 cc. with 90 per cent alcohol and used as a solvent for hot alcohol extraction of the dried residue. The analytical procedure was according to the following scheme:



The extracted fractions were made up in their respective solvents and aliquot portions taken for phosphorus and nitrogen determinations. The remaining portions with the exception of the portion soluble in ether only were titrated against 0.5 *N* alcoholic KOH from a microburet, using phenolphthalein indicator. A known excess of alkali was added, and the solutions were refluxed for 1 hour to effect saponification; the free KOH was back-titrated against 0.5 *N* HCl. The extracted residue was dried at 95° C, weighed, and portions were analyzed for nitrogen, ash and phosphorus. Rubber was determined by refluxing in warm chloroform, filtering cool into a large excess of acetone. The precipitated rubber was gathered together, dried, and weighed. The acetone was evaporated to dryness, and the small amount of acetone-soluble residue was determined.

To determine the amount of the components separable from the yellow fraction in relation to the amounts in the whole latex and its derived yellow fraction, similar analyses were performed as described above. About 600 grams

TABLE 1

SEPARABLE MATERIAL FROM THE YELLOW FRACTION

			%	Acid value	Saponification value	% N	% P
Aqueous-alcohol extract	Ether-solubles	Alcohol soluble	17.5	7.8	18.8	0.12	0.094
		Non-alcohol soluble	2.0	—	—	0.02	0.023
	Non-ether solubles	Alcohol soluble	13.9	11.1	4.2	0.32	0.102
		H_2O soluble	10.1	7.0	3.2	0.10	0.054
Residue	Rubber		16.4				
	Ash (KCl)		8.2	(7.8)			0.034
	Resin		5.1				
	Protein (by N)		19.8			3.2	
			93.0	25.9	26.2	3.76	0.307

of fresh latex was weighed and a weighed portion of 20 grams was coagulated in alcohol. The rest was centrifuged and the yellow fraction obtained (about 100 grams) was weighed. A 10-gram portion of this was precipitated in alcohol. The remainder was subjected to dilution with salt solution and the recentrifugation process previously described, the separable material being added to alcohol.

In the same manner, the determination of the magnesium content was carried out on a separate sample.

Analytical results are tabulated below. All percentages are expressed on the total solids content, which in the case of the separable material was determined by adding the weight of the 90 per cent-alcohol extract to the weight of dried extracted residue. For convenience, the acid values and saponification values are expressed as milligrams of KOH per gram of solids.

Analysis of the separable materials from the yellow fraction shows that its solid content is composed mainly of nonrubber substances.

These are mostly extractable by the 90 per cent alcohol, and rather less than half are soluble in ether. If the acid values and the saponification values of the

TABLE 2

EXTRACTABLES IN WHOLE LATEX, YELLOW FRACTION, AND MATERIAL SEPARABLE FROM YELLOW FRACTION

	% on total solids	Total amount	% P	Total P	Acid value	Total acid value	Saponification value	Total saponification value
Whole latex								
650 g. = 276 g. solids								
Ether solubles	1.95	5.4	0.028	0.077	0.53	146	3.5	964
Aqueous alcohol solubles	6.60	18.2	0.021	0.058	2.9	800	1.3	360
Yellow fraction								
121 g. = 23 g. solids								
Ether solubles	5.4	1.3	0.060	.014	1.9	44	7.1	163
Aqueous alcohol solubles	24.1	6.0	0.170	0.039	18.6	429	8.4	194
Separable material from Y. F.								
60.5 g. = 1.43 g. solids								
Ether solubles	18.9	0.27	0.131	0.0019	5.2	7.4	19.5	28.9
Aqueous alcohol solubles	49.3	0.71	0.504	0.0072	35.0	50.1	13.0	18.6

ether-solubles are expressed as oleic acid, the phosphorus as phosphoric acid, and the nitrogen as choline, it can be supposed to consist mainly of free and combined fatty acids. The combined fatty acids are present presumably as lipids, with a small percentage of phospho-lipids. The alcohol and water solubles, which have been found to vary somewhat in content, must consist to a great extent of free acid. Assuming an equivalent weight of about 200, half of the content would be accounted for as acid. The water solubles formed a syrupy residue when dry, which could be crystallized from acetone and water, and resembled quebrachitol in appearance. It did not, however, have a definite melting point. The substance was not a sugar or a sugar derivative. It had no reducing properties before and after hydrolysis with acid. A small amount of a nonalcohol-soluble substance remaining in the extracted rubber and protein residue, which was soluble in acetone, may well be a rubber derivative or precursor. The small amount of mineral matter in the extracted residue was found to consist almost entirely of potassium chloride.

Table 2 gives the relative amounts of the component substances in whole latex, its equivalent amount of yellow fraction, and the total derived separable material. It can be seen that only a small fraction of the ether, alcohol, and

TABLE 3

MAGNESIUM CONTENTS

	Total Mg (g.)	% on solids
Original whole latex	0.086	0.027
Yellow fraction	0.044	0.226
Y.F. = 40 times diluted with 2% KCl.	0.016	0.45
Further diluted 16 times with water.	0.0057	0.38

water solubles of the original whole latex is present in the yellow fraction. Of this, only a small fraction persists in the separable material.

Reviewing this work, it is evident that there is an association between proteins and lipids which gives rise to heavy substances which separate easily under gravity. The nature of this association requires further study. That this complex has enzyme activity is shown by the rapid fall of pH which takes place on standing and no doubt, the fall in pH of latex during the first few hours after tapping is largely due to the changes taking place in the yellow-fraction substances. The interrelationship between these substances is determined by the pH. At a pH greater than 8.5, no yellow fraction can be separated, and, as the pH falls, it is progressively easier to separate. This indicates that the affinity of the units making up the structure is increased by a fall of pH. It can be attributed to anionic/lipid/protein association to give macromolecules which theory supposes depends on the electrostatic forces between charges which are concentrated at a certain point in the component molecules; for example, in proteins, positive at the NH_2 groups and negative at the COOH groups.

It is, therefore, unlikely that in latex concentrating processes, which are always carried out at a high pH, these phenomena have much significance. The measurable difference between whole latex and white-fraction latex (subsequently ammoniated and concentrated), is not very great. There is a tendency for white-fraction latex to have a somewhat lower mechanical stability, and its chemical stability may be higher.

ZINC OXIDE TESTING OF LATEX *

E. W. MADGE, H. M. COLLIER, AND J. L. M. NEWNHAM

DUNLOP RUBBER CO., LTD., FORT DUNLOP, BIRMINGHAM, ENGLAND

Over the last twenty years, tests of various types, many of them empirical, have been proposed for testing the stability of latex[1].

Some have been standardized, such as those for KOH number and mechanical stability, and these describe certain aspects of the stability problem. There has, however, been a general desire to devise what has come to be known as a chemical stability test; the implication is that such a test would bear a closer relation to the processing behavior of latex, particularly in those processes where there are pH changes during formation of the coagulum and where the particles are in one way or another ionically destabilized or coagulated.

Certain difficulties immediately present themselves. Processes differ widely in their operating conditions, so that process interpretation from any one chemical stability test is contentious. Part of the contention has been due to the adoption of empirical end-point determinations, so that the conditions of a single process are inordinately favored.

The obvious means of attacking the general problem is to deal adequately with the allied problem of zinc sensitization of latex, since zinc oxide is an active component of the majority of latex mixings. Moreover, in processes which are more susceptible to stability variation, such as those involving hot or cold gelling (and such processes are responsible for the largest consumption of latex today), zinc plays a recognizable and powerful role.

The destabilization of ammonia-preserved latex by zinc has been a problem of great difficulty, not only because of the varied nature of the nonrubber components of the latex, but also because of the complication introduced by the way in which zinc forms chemical complexes with ammonia and other components of a latex, the composition of these complexes[2] varying with pH.

Zinc oxide destabilizes ammonia-preserved latex partly by ionic adsorption of positive zinc or zinc ammine ions on the negatively charged rubber globules and partly through the formation of zinc soaps[3].

Zinc oxide destabilization is, therefore, contingent on the presence of ammonium salts in the latex, both those which facilitate the solubilization of zinc oxide and the ammonium salts of long-chain fatty acids which react to precipitate zinc soaps. Other nonrubber components of latex, for example, proteins, interact with zinc, but it is believed that, in gelling processes for mixings containing zinc oxide, the main gelling influence is through the solubilizing of zinc and subsequent formation of zinc soaps.

ZINC OXIDE THICKENING OF LATEX AND THE ZOT TEST

The ZOT test for latex was described many years ago[4], and it records the extent of thickening over a measured period caused by zinc oxide in a latex of

* Reprinted from the *Rubber World*, Vol. 131, No. 6, pages 776–780, March 1955. This paper was presented at the Third Rubber Technology Conference, London, June 22–25, 1954. H. M. Collier is now resident at the Dunlop Research Center, Batang Malaka, Malaya.

very low ammonia content (0.05 per cent). This test has largely had a qualitative rather than a quantitative significance, due partly to the fact that the method of viscosity measurement employed becomes increasingly inaccurate as the latex thickens. Figure 1 shows clearly the variation of viscosity with rate of shear when appreciable thickening with zinc oxide takes place. The determinations were made using a Ferranti viscometer[5].

In addition small variations of pH give rise to large variations in the rate of thickening under the conditions of test, i.e., at ammonia content approximately 0.05 per cent (pH 9), (Figure 2).

Nevertheless, even with the qualitative results obtainable from the standard ZOT test, it was thought that, for extremes of zinc sensitivity, the relative variations in the common tests of ZOT, KOH number, and electrical conductiv-

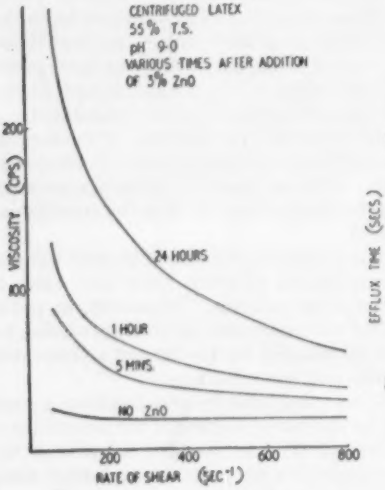


FIG. 1.—Effect of rate of shear on the viscosity of zinc oxide-treated latex.

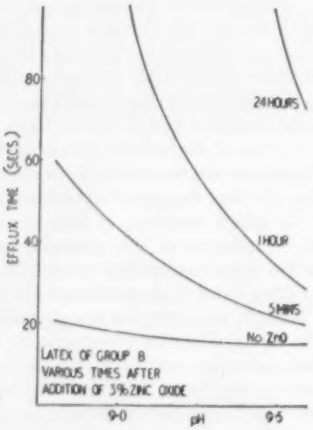


FIG. 2.—Effect of pH on viscosity and rate of thickening of zinc oxide-treated latex.

ity would be significant. Figure 3 shows a plot of conductivity against KOH number for three groups of latexes, A, B, and C. A and B are centrifuged concentrates, and C electrodecanted concentrates. The individual points represent separate bulk shipments of latex.

Murphy[6] has accounted for the higher KOH number of electrodecanted over centrifuged latex by the fact that the electrodecanted latex contains a higher proportion of small particles and consequently a greater proportion of adsorbed nonrubber components.

Murphy[6] and Madge[1] have discussed the relation between electrical conductivity and KOH number. Ammonium salts contribute both to KOH number and to conductivity. Ammonium salts of volatile acids increase conductivity more than the ammonium salts of fatty acids; while salts of strong bases raise conductivity, with little effect on KOH number. Comparison of KOH number and conductivity in Figure 3 for latexes A, B, and C shows the previ-

ously recognized general linear relation, but with significant differences for each latex group. The interpretation of these differences is that the C latexes contain a higher proportion of soap than do the B latexes, and the A latexes a higher proportion of ionic material than the B latexes. This is in agreement with van den Tempel's analyses[7], and fits in qualitatively with the mechanical stability figures.

THE EFFECT OF ADDED SOAP ON THE ZINC OXIDE THICKENING OF LATEX

It has already been shown[6] and may be inferred from the above that the presence of small amounts of soap reduces the ZOT; while elsewhere[3] it has

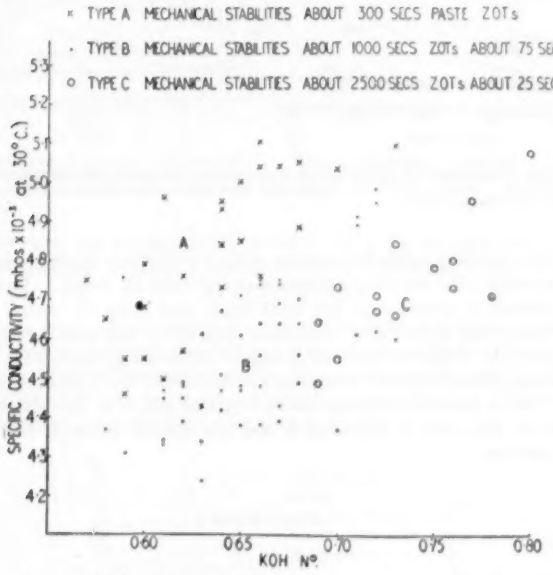


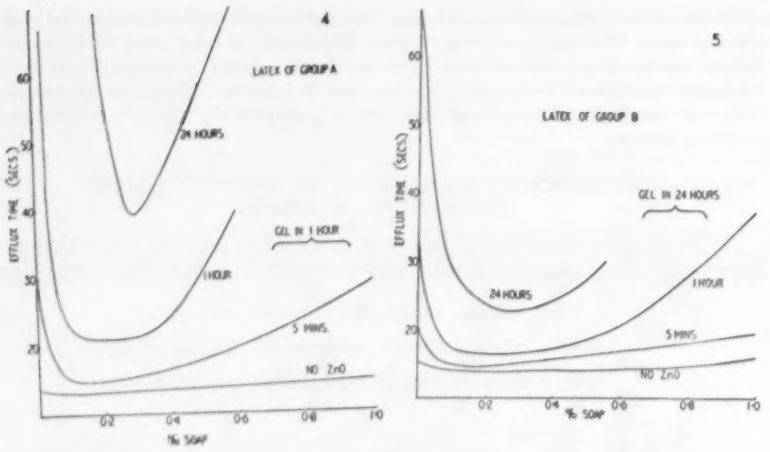
FIG. 3.—Relation between KOH numbers and electrical conductivities of latexes of different ZOT type.

been demonstrated that the presence of appreciable amounts of soap promotes gelling by the formation of zinc soaps.

It was, therefore, necessary to carry out a viscosity study of latexes containing zinc oxide to which increasing amounts of soap were added beforehand.

Figures 4, 5, and 6 show the paths of thickening for typical latexes of groups A, B, and C. In each case the latex was reduced to pH 9 by formalin addition. Increasing amounts of sodium castor-oil soap were added, followed by 3 per cent of zinc oxide on the rubber added as a 50 per cent dispersion. Dilutions were adjusted to give a constant total solids concentration. The curves shown in Figures 4, 5, and 6 represent viscosity determinations made before and five minutes, one hour, and 24 hours after the zinc oxide addition.

The striking feature about these three sets of curves was the fact that with increasing soap additions the viscosity always passed through a minimum.



FIGS. 4 (left) and 5.—Variation of viscosity and rate of thickening of zinc oxide-treated latexes with sodium castor-oil soap content. Latexes at pH 9.0, 55 per cent total solids, viscosities determined various times after addition of 3 per cent zinc oxide.

Latex A gave considerable thickening with a minimum in the neighborhood of 0.3 per cent soap; the minimum became sharp after 24 hours. Latex B gave a broad minimum at about 0.25 per cent soap, and latex C, which only gave slight thickening, had a viscosity minimum nearer 0.1 per cent of soap.

At a higher pH (10.2) a latex of group B containing zinc oxide and 1 per cent ammonium nitrate showed a similar minimum for the viscosity/soap curve (Figure 7). As in the experiments carried out at pH 9 in the absence of ammonium nitrate, the rate of thickening had the lowest value at the minimum point of the curves.

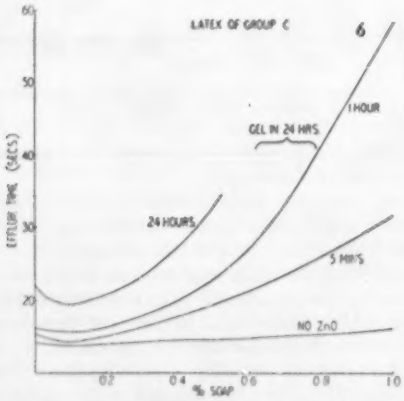


FIG. 6.—Variation of viscosity and rate of thickening of zinc oxide-treated latexes with sodium castor-oil soap content. Latexes at pH 9.0, 55 per cent total solids, viscosities determined various times after addition of 3 per cent zinc oxide.

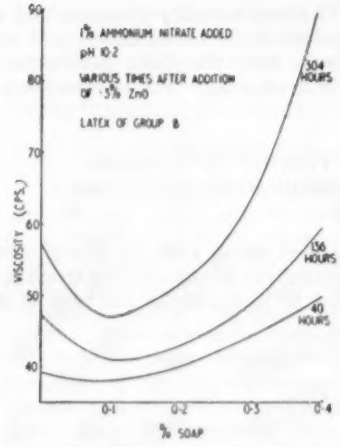


FIG. 7.—Variation of viscosity and rate of thickening of a zinc oxide-treated latex containing ammonium nitrate with sodium castor-oil soap content.

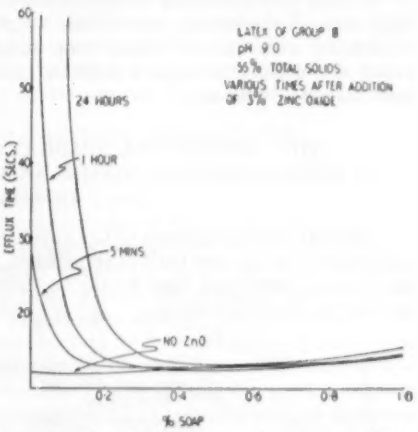


FIG. 8.—Variation of viscosity and rate of thickening of a zinc oxide-treated latex with Vulcastab-LW content.

EFFECT OF DIFFERENT SOAPS ON THE SHAPE OF THE VISCOSITY/SOAP CURVE FOR LATEX CONTAINING ZINC OXIDE

Viscosities were measured under the conditions described in the previous experiments for a zinc oxide-containing latex of group B, to which were added, prior to the zinc oxide, increasing amounts of sodium castor-oil soap, a nonionic soap Vulcastab-LW[8], and ammonium oleate, respectively. The results which were then obtained are shown in Figures 5, 8, and 9.

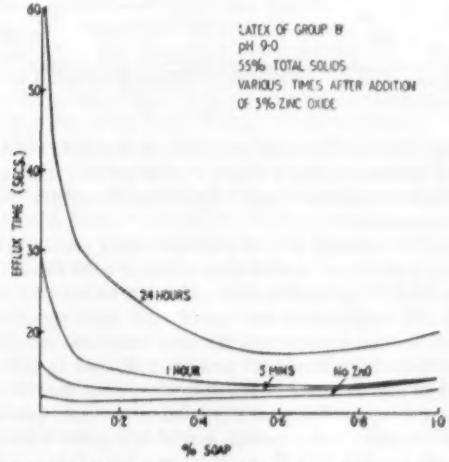
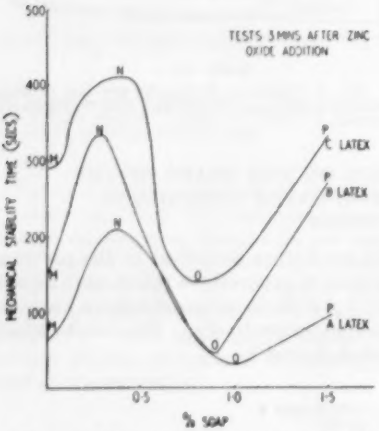


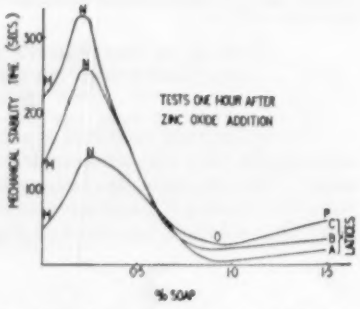
FIG. 9.—Variation of viscosity and rate of thickening of a zinc oxide-treated latex with ammonium oleate content.

Sodium castor-oil soap additions showed a sharp viscosity minimum and a high rate of thickening; a nonionic soap substantially no minimum and no thickening with time at higher soap additions; while the oleate gave a very broad minimum and again a positive rate of thickening. The nonionic soap does not react with zinc.

THE MECHANICAL STABILITY TESTING OF LATEXES CONTAINING ZINC OXIDE AND INCREASING ADDITIONS OF SOAP

Viscosity determinations of the type described above, although giving most unexpected results, are tedious to perform, are subject to quantitative errors for the reasons described, and would be difficult to formulate as the basis of a method for routine testing.





FIGS. 10 (left) and 11.—Variation of mechanical stability with sodium castor-oil soap content of typica latexes of groups A, B, and C treated with zinc oxide. Latexes at pH 9.2–9.3, 55% total solids, 3% zinc oxide added.

The standard Dunlop/Klaxon mechanical stability test apparatus[9] was therefore applied to the systems under investigation, and quicker and more clearly defined results were obtained. Transient structural viscosity effects do not influence these results.

The method of experiment was to add increasing amounts of sodium castor-oil soap to a latex, then 3 per cent of zinc oxide as a 50 per cent dispersion, and to determine the M.S.T. at 14,000 r.p.m. three minutes and one hour after the addition. Final pH values were measured, and were approximately constant at 9.3. The M.S.T. was determined at room remperature (20° C).

The curves obtained for latexes of groups A, B, and C were striking, and are shown in Figures 10 and 11. As in the viscosity/soap curves, a sharp change of slope occurred at a soap addition of approximately 0.25 per cent. In contradistinction to the viscosity/soap curves, the M.S.T. passed through a maximum.

Figure 12 shows similar M.S.T./soap curves for a latex of group B to which 0.2 per cent ammonium nitrate was added originally.

It was observed in all cases that, before the maximum of the M.S.T./soap curve was reached, the end point of the M.S.T. test was characteristic of that normally experienced with standard untreated concentrate. Beyond the maximum of the M.S.T./soap curve, the end point sharpened considerably, leading to a more rapid and complete coagulation as the soap addition increased.

INTERPRETATION OF THE M.S.T./SOAP CURVES

There have been several attempts to carry out mechanical stability tests in the presence of zinc oxide or other chemical destabilizer[10].

These have, however, led to no explanation of the properties of a latex, partly because of lack of knowledge of the effects of pH variation and partly because knowledge of the part played by soap in the sensitization of zinc oxide-containing mixings was lacking, or at least incomplete. Researches during the last few years have done much to provide the missing data, and one of the objects of the present investigation has been to understand in much more detail the effect of the zinc oxide/soap interaction on stability. The matter is of fundamental importance, not only because of the general use of zinc oxide in latex mixings, but because all latex mixings contain a quantity of soap of natural origin or added by way of a dispersion stabilizer or frothing aid.

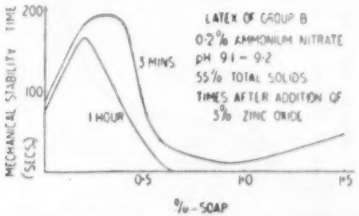


FIG. 12.—Variation of mechanical stability of zinc oxide-treated latex containing ammonium salt, with sodium castor-oil soap content.

For the purpose of comparing latexes, obviously only one soap should be used. Most of the work has, therefore, been carried out with castor-oil soap, partly because it is a favored addition in latex processes.

In the curves of Figures 10 and 11 it is reasonable to assume that the increase in stability over the first part MN of the curves is directly associated with a change of the surface protection of the particle. It is tempting to assume that this is simply an adsorption of surface-active soap on the latex particles and that the maximum *N* corresponds to the point where they are fully covered. It is difficult to understand, however, why the addition of zinc oxide does not lead to normal formation of zinc soap at the particle interface with consequent destabilization. Be that as it may, there is a definite qualitative as well as quantative change in the system after the maximum *N* has been passed, and presumably increasing amounts of soap are now available in the serum and free to react with the zinc or zinc ammine ions present.

The portion NO of the curves corresponds, therefore, to a destabilization by the zinc soap formed. The minimum O of curve 10 can be taken as the point where the available zinc is satisfied by the added soap, and thereafter further soap additions give rise to increased stabilization, as shown by the portion OP of curve 10. If more zinc is available, as in the case of the one hour curve (Figure 11), the portion OP, as might be expected, is substantially flat.

The maximum N was found not to be sensitive to pH variation over the range pH 9 to 10. The slope NO was more sensitive; hence a given pH could be selected for carrying out the test. The results given in Figures 10, 11, and 12 were obtained at pH 9.1–9.3.

EFFECT OF DIFFERENT SOAPS ON THE SHAPE OF THE M.S.T./SOAP CURVE FOR LATEX CONTAINING ZINC OXIDE

It has already been demonstrated that there is a pronounced difference after zinc oxide addition in the viscosity behavior of latexes to which increasing amounts of soaps of different types are added (Figures 5, 8, and 9). Latexes containing castor-oil soap are the most pronounced in their thickening. The effect of a nonionic soap that does not react with zinc is clear, but it is probable that, since both ammonium oleate and castor-oil soap lead to the formation of

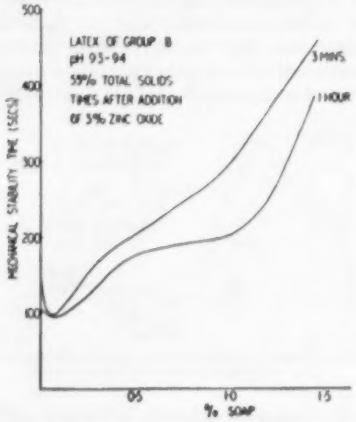


FIG. 13.—Variation of mechanical stability of zinc oxide-treated latex with Vulcastab-LW content.

zinc soaps, there must be some specific destabilizing quality of the particular zinc soap formed when castor oil soap is used. In this connection, the difference is hydrophilic nature of the two soap molecules is probably of importance.

In a rather similar way to the viscosity relations, castor-oil soap was found to have a specific effect on the M.S.T. relations, and the characteristic zinc soaps were found to be strongly destabilizing. Figures 13 and 14 show M.S.T./soap curves for both nonionic (Vulcastab-LW) and ammonium oleate soaps in the presence of zinc oxide, and it will be seen that these are different in type from those of castor-oil soap (Figures 10 and 11). Both oleate and nonionic soap give chiefly a stabilizing effect.

A qualitative difference of behavior was demonstrated when, instead of a zinc oxide addition, an addition of zinc ammine solution was made to latex containing castor-oil soap or ammonium oleate. With 0.6 per cent of ammonium oleate present, coagulation did not take place on addition of the ammine solution, but with a similar amount of sodium castor-oil soap present, coagulation was immediate.

It is clear that many of the observations described and discussed in this paper still require further investigation for their clarification and fundamental elucidation.

SUMMARY AND CONCLUSIONS

Viscosity changes in concentrated natural rubber latex under different experimental conditions were investigated with the object of determining the mechanism of zinc oxide thickening and to find reasons for inconsistencies in correlating results of the zinc oxide thickening or ZOT test with other latex tests. It has been found that small variations of the amount of naturally occurring soap are of great importance in the thickening of latex containing zinc oxide, especially at the low ammonia content used for the ZOT test.

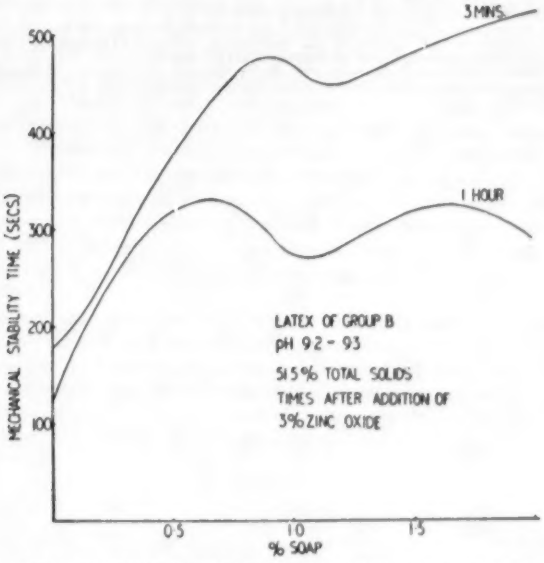


FIG. 14.—Variation of mechanical stability of zinc oxide-treated latex with ammonium oleate content.

The effect of added soap on the ZOT test was found to vary from latex to latex and to be different for different soaps. Less than about 0.3 per cent of various soaps added to latex prior to the zinc oxide reduced the degree and rate of thickening. With more than this amount of soap, the thickening depended on the soap used.

A similar investigation in which the mechanical stability of latexes containing varying amounts of added soap and a standard amount of zinc oxide was measured, showed that the latexes varied anomalously with the amount and the type of soap added.

The results of the work presented in this paper show that new tests for the zinc sensitivity of latexes must take into account a number of hitherto unsuspected factors, particularly when such tests are required to have a bearing on processing behavior.

ACKNOWLEDGMENTS

Acknowledgment is made to Dunlop Rubber Co., Ltd., for permission to publish this paper.

Appreciation is also expressed to D. J. Simcox for considerable assitance in the experimental work described.

REFERENCES

[1] Madge, *Trans. Inst. Rubber Ind.* **28**, 207 (1952).
[2] Wren, *Trans. Inst. Rubber Ind.* **18**, 91 (1942); Panich, Kal'yanova, and Voyutskiĭ, *Kolloid. Zhur.* **12**, 50 (1950); Cassagne, *Rev. gén. caoutchouc* **28**, 39, 105 (1951).
[3] Kraay and van den Tempel, *Trans. Inst. Rubber Ind.* **28**, 144 (1952); Newnham, *Trans. Inst. Rubber Ind.* **29**, 160 (1953).
[4] Murphy, *Proc. Rubber Technol. Conf. London*, **1938**, p. 151.
[5] Model VL, Manufactured by Ferranti, Ltd., Hollinwood, Lancashire, England.
[6] Murphy, *Ind. Eng. Chem.* **44**, 756 (1952).
[7] Van den Tempel, *Trans. Inst. Rubber Ind.* **29**, 312 (1953).
[8] Manufactured by Imperial Chemical Industries, Ltd., Millbank, London, SW 1.
[9] Manufactured by Klaxon, Ltd., London W 11. See Madge, Collier and Duckworth, *Trans. Inst. Rubber Ind.* **28**, 15 (1952); Rubber Chem. & Technol. **25**, 630 (1952).
[10] Bächle, *Kautschuk*, **11**, 219 (1935); Murphy, *Proc. Rubber Technol. Conf. London*, **1938**, p. 151; Davey and Coker, *Trans. Inst. Rubber Ind.* **13**, 368 (1938); Martin, Rubber Chem. & Technol. **19**, 494 (1946); **20**, 606 (1947).

DETERMINATION OF FREE SULFUR IN HARD RUBBER *

C. WYNNE-EVANS

DUNLOP RUBBER CO., LTD., MANCHESTER, ENGLAND

INTRODUCTION

The amount of free sulfur in a vulcanized hard rubber is just as important, and in some cases more important, than that contained in a soft rubber. In order to determine this amount, the methods in use for soft rubbers are, in general, also applicable to hard rubbers.

The usual method is to carry out an acetone extraction and to conduct a bromination on the extract, followed by precipitation with barium chloride, filtration, and ignition, and weighing as barium sulfate[1]. Another method is to take the brominated acetone extract and titrate with barium chloride solution, using tetrahydroxyquinone as indicator[2]. A third method is to acetone extract in the presence of a clean copper spiral, and then remove the copper sulfide so formed with hydrochloric acid, and pass the hydrogen sulfide which is produced through cadmium acetate solution; the cadmium sulfide formed is determined iodometrically[3].

All three methods, together with others[4] in general use, are, unfortunately, lengthy determinations, and in addition have unpleasant oxidations, either with bromine or nitric and perchloric acids. Assuming all goes well, the shortest time in which a result can be obtained is two days, but generally three or even four days are necessary. For purposes of factory control work, this is unsatisfactory, whether the factory is manufacturing hard or soft rubbers.

TABLE 1

Vulcanized soft rubbers Same sample, various cures	Method (% free sulfur)		
	Bromine	Copper spiral	Sodium sulfite
Sample (1)	1.65	1.67	1.65
Sample (2)	1.15	1.21	1.16
Sample (3)	0.84	0.85	0.85
Sample (4)	0.62	0.63	0.62
Sample (5)	0.75	0.76	0.75

In the case of ebonite manufacture, where the amount of free sulfur is of paramount importance, this time lag is a nuisance, and it was because of this that the sodium sulfite procedure[5] was investigated.

In brief, the determination consists of extracting any free or available sulfur with sodium sulfite, and titrating the sodium thiosulfate so formed with iodine, using starch, sodium starch glycollate or thiodene as an indicator. Thiodene has been found to give the best end-point. This method with soft rubbers is known to be speedy and accurate, as the results in Table 1 show, and these compare favorably with the bromine and copper spiral methods.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 31, No. 4, pages 126–131, August 1955.

The mechanism of the reactions is shown in the following equations:

(*a*) $S + Na_2SO_3 = Na_2S_2O_3$

(*b*) $C_6H_4NSCSH + Na_2SO_3 = C_6H_4NSCSNa + NaHSO_3$

(*c*) $2NaOOC(CH_2)_{16}CH_3 + SrCl_2 = Sr(OOC(CH_2)_{16}CH_3)_2 + 2NaCl$

(*d*) $Na_2SO_3 + SrCl_2 = SrSO_3 + 2NaCl$

(*e*) $2C_6H_4NSCSNa + Cd(OOCCH_3)_2 = (C_6H_4NSCS)_2Cd + 2NaOOCCH_3$

(*f*) $Na_2SO_3 + Cd(OOCCH_3)_2 = CdSO_3 + 2NaOOCCH_3$

(*g*) $HCHO + Na_2SO_3 + H_2O = H_2C(OH)SO_3Na + NaOH$

(*h*) $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$

EXPERIMENTAL

As a preliminary experiment, the procedure of Bolotnikov and Gurova[6] modified by Oldham, Baker and Craytor[7], was adopted, using known weights of elemental sulfur, of the order found in unvulcanized hard rubber.

The method adopted was as follows.

X grams of sulfur (pass 100-mesh sieve) were placed in a 400-cc. Underwriter flask, and 100 cc. of 5 per cent sodium sulfite solution, 5 cc. of a 0.1 per cent sodium stearate suspension in water, and approximately 1 gram of paraffin wax were added. The flask was covered with a small watch-glass and heated so as to boil gently for two hours.

TABLE 2

Sulfur used (grams)	Sulfur found (grams)	Percentage of sulfur unextracted
0.0750	0.0748	0.3
0.0500	0.0499	0.2
0.0250	0.0250	—

The glass was removed and 100 cc. of 0.5 per cent strontium chloride solution and 10 cc. of 3 per cent cadmium acetate solution were added, and the precipitates separated by filtration, using a Buchner funnel with suction. Two washings with 75 to 100 cc. portions of a wash solution containing 40 cc. of 3 per cent cadmium acetate solution per liter, were then carried out, and to the filtrate was added, with stirring, 5 cc. of 40 per cent formalin solution, 10 cc. of glacial acetic acid, and 5 cc. of 1 per cent starch solution. Enough crushed ice was added to bring the temperature of the solution bellw 15° C and titration with a standard solution of iodine, to a blue end-point, was carried out.

TABLE 3

	Bromine %	T.H.Q. %	Sodium sulfite %
Mean (nom. 10%)	9.92	9.63	9.93
Standard deviation	0.06	0.11	0.026
Limits 99.7% 3σ	±0.18	±0.33	±0.078
Coeff. of variation	0.60	1.14	0.26

A blank determination was run on the reagents, and this figure, usually 0.2 to 0.3 cc., was substracted from the titrations of the sample, and the results obtained are shown in Table 2.

These figures are promising and show that the concentration of sulfur is of no consequence, providing that there is an excess of sodium sulfite present.

TABLE 4

	Bromine	T.H.Q.	Sodium sulfite
Mean	0.30	0.42	0.45
Standard deviation	0.04	0.008	0.07
Limits 99.7% 3σ	±0.12	±0.024	±0.2
Coeff. of variation	13.33	1.92	15.50

Sulfur was dispersed in a 10 per cent rubber/sulfur master-batch, and 0.250 gram of which, in a finely divided condition, was next used, this being equivalent to 0.0250 gram of sulfur. For comparative purposes, the sulfur was also determined both by the bromine[1] and the tetrahydroxyquinone (T.H.Q.[2]) methods, and the results are shown in Table 3, from which it is seen that there is no significant difference between the bromine and sodium sulfite methods, and that the T.H.Q. method is the least accurate. This inaccuracy follows from the difficulty of getting a clear indication of the end point, due to the high titer of barium chloride involved, even when using the froth as an indication of the end point, as the color of the froth persists over a range of titer.

Attention was then given to vulcanized hard rubber, in which the free sulfur is in general higher than that found in soft rubbers, and in this, and other hard rubber experiments, the weight of sample taken was 2.000 grams.

The results obtained are shown in Table 4.

TABLE 5

	Bromine %	T.H.Q. %	Sodium sulfite %
Mean	0.36	0.42	0.445
Standard deviation	0.06	0.006	0.019
Limits 99.7% 3σ	±0.18	±0.018	±0.057
Coeff. of variation	20	1.5	11

Using a hard rubber with more mineral filler content gave results shown in Table 5. The particle size of the dust for the last two experiments was pass 100 mesh sieve[8].

From both Tables 4 and 5 it can be seen that the T.H.Q. method is the most accurate, but that the sodium sulfite method compares favorably and has an undisputed time advantage.

The reason for the accuracy of the T.H.Q. method is that the end point was sharp, owing to the low titer of barium chloride.

EFFECT OF PARTICLE SIZE [8]

The results of the sodium sulfite method led to the investigation of the particle size of the ebonite on the results.

The results in Table 6 show that the particle size, as would probably be expected, is more critical in the case of the sodium sulfite method than in the other two because of the much shorter extraction time.

TABLE 6

Particle size (Same state of cure and same compound)	Bromine % free sulfur	T.H.Q. % free sulfur	Sodium sulfite % free sulfur
Pass 100 mesh	0.22	0.21	0.21
Pass 60 mesh, retained 100	0.22	0.22	0.21
Pass 30 mesh, retained 60	0.22	0.21	0.20
Pass 22 mesh, retained 30	0.21	0.22	0.18
Pass 12 mesh, retained 22	0.22	0.22	0.16
Pass 6 mesh, retained 12	0.18	0.16	0.11

TABLE 7

Time of boiling (hours)	Particle size		Sodium sulfite % free sulfur
	Pass	Retain	
2	100		0.21
	60	100	0.21
	30	60	0.20
	22	30	0.18
	12	22	0.16
	6	12	0.11
3	100		0.21
	60	100	0.21
	30	60	0.21
	22	30	0.22
	12	22	0.21
	6	12	0.13
4	6	12	0.15
5	6	12	0.17
6	6	12	0.17

EFFECT OF LONGER EXTRACTION WITH SODIUM SULFITE

In view of the under extraction of the sulfur in the particle size range (pass 30-mesh retain 60-mesh sieve and coarser), the effect of a longer period of extraction with the sodium sulfite was tried, using the same ebonite as in Table 6, the results being shown in Table 7.

Table 7 shows that a state of extraction comparable with the bromine and T.H.Q. methods is reached at 3 hours and up to a particle size of pass 12 retain 22. A coarser particle size results in incomplete extraction of sulfur even after 6 hours' extraction time. In view of this length of time, it was decided not to pursue an extraction period of more than 3 hours, or a coarseness greater than pass 12 retain 22.

EFFECT OF CONCENTRATION OF SODIUM SULFITE

The standard sulfite method was modified to a solution strength of 7.5 per cent sodium sulfite, and the amounts of all the other reagents were proportionately increased by 50 per cent. The results shown in Table 8 were obtained using various samples of a microporous hard rubber, with high rubber content.

These results show that, when using a hard rubber of free sulfur content greater than 2 per cent (even with microporous hard rubber, which should help the extraction), and using 7.5 per cent sodium sulfite solution, the extraction is still not complete at 2 hours, and as the 5 per cent sodium sulfite agrees at 3 hours' extraction with the stronger sulfite solution, there appears to be little or no advantage in using 7.5 per cent strength.

TABLE 8

	Time of boiling (hours)	5% Sulfite	7.5% Sulfite
(1)	2	2.36	2.36
	3	2.93	2.94
(2)	2	1.24	1.24
	3	1.24	1.24
(3)	2	1.00	0.99
	3	1.07	1.07
(4)	2	1.31	1.34
	3	1.54	1.54

The following standard method for the determination of free sulfur in vulcanized hard rubber is, therefore, recommended.

Two grams of hard rubber filings of particle size no coarser[8] than pass 12 and retain 22 are placed in a 400 cc. underwriter's flask, and 100 cc. of 5 per cent sodium sulfite solution, 5 cc. of a 0.1 per cent sodium stearate suspension in water, and approximately 1 gram of paraffin wax are added. The flask is covered with a small watch-glass and heated so as to boil gently for 3 hours. The glass is removed and 100 cc. of 0.5 per cent strontium chloride solution and 10 cc. of 3 per cent cadmium acetate solution are added, followed by separation of the precipitates by filtration, using a Buchner funnel with suction. This is washed with two 75 to 100 cc. portions of a wash solution containing 40 cc. of 3 per cent cadmium acetate solution per liter, and to the filtrate is added, with stirring, 5 cc. of 40 per cent formalin solution, 10 cc. of glacial acetic acid and 5 cc. of 1 per cent thiodene solution. Enough crushed ice is added to bring the temperature of the solution below 15° C, and the solution is then titrated with a standard solution of iodine to a blue end-point. A blank determination is run on the reagents and this figure, usually 0.2 to 0.3 cc., is subtracted from the titrations on the samples. 1 cc. 0.1 *N* iodine = 0.003206 gram sulfur.

It should be noted that if mercaptobenzothiazole is known to be absent, the treatment with cadmium acetate solution may be omitted.

It is essential that the reagents in the above method should be added separately, in the order stated.

As a sulfur control for the mill personnel, the method may be used by taking 0.25 gram of finely unvulcanized milled sheeting and carrying out the above standard method. This will give the added weighed sulphur rapidly and accurately.

SUMMARY

The volumetric method for the determination of sulfur by means of aqueous sodium sulfite has been adapted for the determination of free sulfur present in hard-rubber vulcanizates.

This work was carried out because there was not a speedy free sulfur method applicable to hard rubbers, and the investigation has shown that, by the use of aqueous sodium sulfite, it is possible to obtain reliable and extremely accurate free sulfur results in a little over three hours, against the usual three to four days by other methods which are discussed.

ACKNOWLEDGMENTS

The author wishes to express his thanks to United Ebonite & Lorival, Ltd., and the Dunlop Rubber Co., Ltd., for facilities for carrying out the work and for permission to publish. Also to Derek Lee for his help during the latter stages of the work.

REFERENCES

[1] Methods of Testing Vulcanized Rubber, B.S.S. 903: **1950**, 33.
[2] Scott, "Standard Methods of Chemical Analysis", 5th Ed., Vol. 1, p. 919.
[3] Methods of Testing Vulcanized Rubber, B.S.S. 903: **1950**, 35.
[4] Mackay and Avons, *Trans. Inst. Rubber Ind.* **16**, 117, (1940); Methods of Testing Vulcanized Rubber, B.S.S. 903; **1950**, 34.
[5] Bolotnikov and Gourova, *J. Rubber Ind.* (U.S.S.R.) **10**, 61 (1933); Rubber Chem. & Technol. **8**, 87 (1935); Oldham, Baker, and Craytor, *Ind. Eng. Chem. Anal. Ed.* **8**, 41 (1936); Pande and Ramakrishnan, *India-Rubber J.* **121**, 803, 807 (1951); Poulton, F. C. J., private communication.
[6] Bolotnikov and Gourova, *J. Rubber Ind.* (U.S.S.R.) **10**, 61 (1933); Rubber Chem. & Technol. **8**, 87 (1935).
[7] Oldham, Baker, and Craytor, *Ind. Eng. Chem. Anal. Ed.* **8**, 41 (1936).
[8] Test Sieves, B.S.S. 410: 1943.

PROMOTERS FOR THE REACTION OF RUBBER WITH CARBON BLACK

KENNETH W. DOAK, GEORGE H. GANZHORN, AND BERNARD C. BARTON

GENERAL LABORATORIES, UNITED STATES RUBBER CO., PASSAIC, NEW JERSEY

An article of the title above and by the authors above was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 28, No. 3, pages 895–905, July–September 1955.

In the text of page 903, the fifth paragraph contains the sentence: "Channel black also suppresses gel formation during heating of GR-S[26] . . .". This reference No. 26 should be No. 27, i.e. the sentence should read: "Channel black also suppresses gel formation during heating of GR-S[27] . . .".

The references on page 905 are incorrect, and the reader of this article should disregard this list of references and use the following correct references.

REFERENCES

[1] Gerke, Ganzhorn, Howland, and Smallwood, U. S. patent 2,118,601 (May (1938).
[2] Bradley, U. S. patent 2,239,659 (April 1941).
[3] Gessler, *Rubber Age* (N. Y.) **74**, 59 (1953); Barton, Ganzhorn, and Smallwood, *J. Polymer Sci.* **12**, 487 (1954).
[4] Dannenberg, *Ind. Eng. Chem.* **44**, 813 (1952).
[5] Barton, Ganzhorn, and Smallwood, *J. Polymer Sci.* **12**, 487 (1954).
[6] Howland, U. S. patents 2,315,855 and 2,315,856 (1943).
[7] Gessler and Ford, *Rubber Age* (N. Y.) **74**, 397 (1953).
[8] Howland, U. S. patent 2,315,857 (1943).
[9] Gerke, U. S. patent 2,315,850 (1943).
[10] Gerke, U. S. patent 2,315,849 (1943).
[11] Barton, U. S. patent 2,658,092 (Nov. 1953).
[12] Gerke, Ganzhorn, Howland, and Smallwood, U. S. patent 2,118,601 (1938); Barton, Ganzhorn, and Smallwood, *J. Polymer Sci.* **12**, 487 (1954).
[13] Doak, U. S. patent 2,676,944 (April 1954).
[14] Doak, K. W., U. S. patents pending.
[15] Barton, U. S. patent 2,689,842 (Sept. 1954).
[16] Gessler, *Rubber Age* (N. Y.) **74**, 59 (1953); Barton, Ganzhorn, and Smallwood, *J. Polymer Sci.* **12**, 487 (1954); Rehner and Gessler, *Rubber Age* (N. Y.) **74**, 561 (1954).
[17] Gessler, *Rubber Age* (N. Y.) **74**, 59 (1953).
[18] Zapp and Gessler, *Rubber Age* (N. Y.) **74**, 243 (1953); Barton, Ganzhorn, and Smallwood, *J. Polymer Sci.* **12**, 487 (1954).
[19] Gerke, Ganzhorn, Howland, and Smallwood, U. S. patent 2,118,601 (May 1938); Parkinson and Blanchard, *Trans. Inst. Rubber Ind.* **23**, 259 (1948); Rehner and Gessler, *Rubber Age* (N. Y.) 74, 561 (1954).
[20] Farmer, *Trans. Faraday Soc.* **42**, 228 (1946); Bolland and Gee, *Trans. Faraday Soc.* **42**, 236, 244 (1946); Farmer and Moore, *J. Chem. Soc.* (London), **1951**, pp. 131, 142, 149; Marek, *Ind. Eng. Chem.* **45**, 2006 (1953); Braden, Fletcher, and McSweeney, *Trans. Inst. Rubber Ind.* **30**, 44 (1954).
[21] Smith and Schaeffer, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 403; Villars, *J. Am. Chem. Soc.*, **69**, 214 (1947); **70**, 3655 (1948).
[22] Stearns and Johnson *Ind. Eng. Chem.* **43**, 146 (1951); Watson and Parkinson, *Rubber Age* (N. Y.) **73**, 502 (1953).
[23] Bartlett, Hammond, and Kwart, *Discussions Faraday Soc.* **2**, 342 (1947).
[24] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); Alfrey, Hendricks, Hershey, and Mark, *India Rubber World* **112**, 377 (1945); Tobolsky, *Discussions Faraday Soc.* **2**, 384 (1947); Sturgis, Baum, and Trepagnier, *Ind. Eng. Chem.* **39**, 64 (1947); Farmer and Moore, *J. Chem. Soc.* (London) **1951**, pp. 131, 142, 149; Braden, Fletcher, and McSweeney, *Trans. Inst. Rubber Ind.* **30**, 44 (1954).
[25] Farmer and Sundralingam, *J. Chem. Soc.*, **1942**, p. 121; Farmer, Bloomfield, Sundralingam, and Sutton, *Trans. Faraday Soc.* **38**, 348 (1942); Bolland and Gee, *Trans. Faraday Soc.* **43**, 236, 244 (1946); Marek, *Ind. Eng. Chem.* **45**, 2006 (1953); Braden, Fletcher, and McSweeney, *Trans. Inst. Rubber Ind.* **30**, 44 (1954).

[29] George and Walsh, *Trans. Faraday Soc.* **42**, 94 (1946); Tobolsky, *Discussions Faraday Soc.* **2**, 384 (1947); Kendall, *Ind. Eng. Chem.* **43**, 452 (1951).
[27] White, Ebers, Shriver, and Breck, *Ind. Eng. Chem.* **37**, 770 (1945).
[28] Sweitzer and Lyon, *Ind. Eng. Chem.* **44**, 125 (1952); Lyon, Burgess, and Sweitzer, paper presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Boston, May 27–29, 1953.
[29] Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Ann.* **551**, 80 (1942); Bloomfield, *J. Chem. Soc.*, **1944**, p. 114.
[30] Robertson and Waters, *J. Chem. Soc.* (London) **1947**, p. 492.
[31] Fields, *J. Am. Chem. Soc.* **76**, 2709 (1954).
[32] Fisher, *Ind. Eng. Chem.*, **31**, 1381 (1939).
[33] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); Rehner and Flory, *Ind. Eng. Chem.* **38**, 500 (1946).
[34] Arnold and Collins, *J. Am. Chem. Soc.* **61**, 1407 (1939); Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); Rehner and Flory, *Ind. Eng. Chem.* **38**, 500 (1946).
[35] Rehner and Flory, *Ind. Eng. Chem.* **38**, 500 (1946).
[36] Stearns and Johnson, *Ind. Eng. Chem.* **43**, 146 (1951).
[37] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); Selker and Kemp, *Ind. Eng. Chem.* **36**, 16 (1944); Armstrong, Little, and Doak, *Ind. Eng. Chem.* **36**, 628 (1944).

INDEX

RUBBER CHEMISTRY AND TECHNOLOGY
VOLUME XXVIII, 1955

AUTHOR INDEX

Page

ALEKSANDROVICH, KH. M. See STAROBINETS, G. L.

AMBERLANG, J. C., AND SMITH, G. E. P., JR. Behavior of reclaiming agents in sulfur and nonsulfur GR-S vulcanizates 322

AMERONGEN, G. J. VAN. Effect of fillers on the permeability of rubber to gases 821

ANDERSEN, D. E., AND KOVACIC, PETER. Aging stability of Neoprene latex. Relation between cross-linking and hydrolysis of allylic chlorine 628

BAADER, TH. The Mooney viscometer 588

BAKER, H. C. Vulcanizing variability of natural rubber in pure-gum and carbon black compounds 570

BARBIER, JEAN. Study of permeability to gases. Mixtures of natural rubber and other elastomers 814

BARTENEV, G. M. Laws of unidimensional compression and stretching of rubber ... 19

———. Representation of the mechanical properties of high-polymers by the model method 66

———, RATNER, S. B., NOVIKOVA, N. M., AND KONENKOV, K. S. Testing of rubber for its low-temperature stability by measurement of the loss of elasticity 711

BARTON, BERNARD C. See DOAK, KENNETH W.

———, SMALLWOOD, HUGH M., AND GANZHORN, GEO. H. Chemistry in carbon black dispersion 202

BASS, S. I. See KUZMINSKII, A. S.

BEATTY, J. R. See JUVE, A. E.

———, AND JUVE, A. E. Simple objective method for estimating low concentrations of ozone in air 608

BENNETT, R. B., AND SMITH, G. E. P., JR. Relation of oxygen to the activity of GR-S reclaiming agents 308

BEST, L. L., AND MORRELL, S. H. Effect of sulfuric acid coagulation on properties of natural rubber 1185

BEVILACQUA, E. M. Water-soluble acids of the latex of Hevea brasiliensis 657

BINDER, JOHN L. Microstructures of polybutadienes and butadiene-styrene copolymers 121

BILLUART, (MRS.) M. See PINAZZI, C. P.

BLANCHARD, A. F. Breakage of rubber-filler linkages and energy dissipation in stressed rubber 540

BLOKH, G. A., AND SAZONOVA, L. P. Reaction of a thiuram with sulfur 804

BOISSONAS, CH. G. See EHRBAR, J. P.

BOONSTRA, B. B. S. T. See DANNENBERG, E. M.

BRADEN, M., FLETCHER, W. P., AND MCSWEENEY, G. P. Vulcanization of rubber by organic peroxides 190

BROWN, HAROLD P., AND GIBBS, CARLIN F. Carboxylic elastomers 937

BUECHE, A. M. Curing of silicone rubber with benzoyl peroxide 865

BUIST, J. M. Aging and weathering of rubber 230

BULGIN, D., AND WRATTEN, R. Measurements of steady flow characteristics of rubber at high rates of shear 534

Page

CHAFFUIS, M. M., POLLEY, M. H., AND SCHULZ, R. A. Reinforced rubber stocks under the electron microscope 253

CHARLESBY, ARTHUR. Cross-linking of rubber by pile radiation 1

CHERTKOVA, V. F. See KUZMINSKII, A. S.

COLLIER, H. M. See MADGE, E. W.

CORTYL-LACAU, (MME.) L. Degradation of high polymers. Scission reactions in the oxidation of GR-8 in solution.

I. Experimental part 746

II. Theoretical part and a kinetic study ... 758

CRAMPSEY, EDWARD, GORDON, MANFRED, AND SHARPE, JOHN W. Electron-microscopic study of the locul of a latex reaction 623

———, AND TAYLOR, JAMES S. Kinetics and mechanism of hydrochlorination of synthetic and natural polyisoprene latex . 288

DANIELS, R. D. See GEHMAN, S. D.

DANNENBERG, E. M., AND BOONSTRA, B. B. S. T. Performance of carbon blacks. Influence of surface roughness and porosity 878

DECKER, GEORGE E. See ROTH, FRANK L.

DOAK, KENNETH W., GANZHORN, GEO. H., AND BARTON, BERNARD C. Promotors for the reaction of rubber with carbon black 895, 1164

DOGADKIN, B. A. See LUKOMSKAYA, A. I.; REZNIKOVSKII, M. M.

———, AND LUKOMSKAYA, A. Structure and dielectric properties of rubber mixtures containing carbon black 891

DRAKE, G. W. Some osmotic measurements of the molecular weight of a high-molecular fraction of rubber hydrocarbon 504

EBERT, G., AND WEIDNER, V. Abrasion and slippage 1082

EDWARDS, D. C., AND STOREY, E. G. Ozone resistance of Butyl vulcanizates 1096

EHRBAR, J. P., AND BOISSONNAS, CH. G. Thermal effect in the elongation and relaxation of rubber 675

ERMOLENKO, N. F. See ERMOLENKO, I. N.

ERMOLENKO, I. N., MAZEL, M. I., AND ERMOLENKO, N. G. Importance of the polar component of mixed fluids in the swelling of vulcanizates 833

FARMER, E. H., FORD, J. F., AND LYONS, J. A. Interaction of sulfur and sulfur compounds with olefinic substances. VII. Low-temperature sulfuration of trialkylethyleneswith hydrogen sulfide-sulfur dioxide and with a sulfur-zinc dithiocarbamate system 470

FETTES, E. M., JORCZAK, J. S., AND PANEK, J. R. Mechanism of vulcanization of polysulfide rubbers 139

FIELD, J. E., WOODFORD, AND GEHMAN, S. D. Infrared study of oxidation of elastomers . 770

FLETCHER, W. P. See BRADEN, M.

FORD, J. F. See FARMER, E. H.

FROMANDI, GUIDO. See ROELIG, HERMANN.

Page

GAGINA, K. See SANDOMIRSKIĬ, D. M.
GALIL-OGLY, F. A. See NOVIKOV. A.
GANZHORN, GEO. H. See BARTON, BERNARD C.; DOAK, KENNETH W.
GARTEN, V. A. Free-radical activity of reinforcing rubber fillers 596
GEHMAN, S. D. See FIELD, J. E.
———, AND HOBBS, L. M. Changes in elastomers due to radiation from cobalt^{60}. 12
———, WILKINSON, C. S., JR., AND DANIELS, R. D. Smearing of vulcanized rubber ... 508
GENT, A. N. Crystallization in natural rubber.
II. Influence of impurities 457
III. Filled compounds 460
———. Crystallization and the relaxation of stress in stretched natural-rubber vulcanizates 36
GIBBS, CARLIN F. See BROWN, HAROLD P.
GILS, G. E., VAN AND RESING, W. L. Accelerated coagulation of latex 1193
GLAZEBROOK, R. W., AND SAVILLE, R. W. Reactions of amines and sulfur with olefins. III. The reaction of diethylamine and sulfur with 1,5-diolefins 109
GLAZER, J. Vulcanization of crepe rubber by sulfur monochloride. II. The dilatometric method 850
———, AND SCHULMAN, J. H. Vulcanization of crepe rubber by sulfur monochloride. I. The gelation method 278
GORDON, MANFRED. See CRAMPSEY, EDWARD.
———, AND TAYLOR, JAMES S. Evidence for a hydrochlorination retarder within natural-rubber latex particles 918
———, AND ———. Introduction to the mechanism of the hydrochlorination of rubber 207
GUL, V. E., AND KLITENIK, G. S. Effect of molecular interaction on the light scattering of rubber solutions 494
GUMBRELL, S. M., MULLINS, L., AND RIVLIN, R. S. Departures of the elastic behavior of rubbers in simple extension from the kinetic theory 24

HÄNDLER, F. See KAINRADL, P.
HENDERSON, D. A., AND MCLEOD, L. A. Low-temperature properties of plasticized butadiene-styrene copolymers 557
HENRI-ROBERT, P. Test of the applicability of dielectric loss measurements to the study of the aging of pure-gum rubber mixtures 420
HOBBS, L. M. See GEHMAN, S. D.
HONNOLD, V. R., MCCAFFREY, F., AND MROWCA, B. A. Studies of rubberlike polymers by nuclear magnetism 480
HOWLAND, L. H., AND NISONOFF, ALFRED. Mechanism of formation of cream in GR-S latex 641
HRIVIKOVA, J. See TKÁČ, A.
HUTTON, ALLEN Q., AND NOLLE, A. W. Experimental study of low-frequency effects on the dynamic modulus of a Buna-N rubber 131

IMOTO, MINORU, AND KIRIYAMA, SHIGERU. Studies of the mechanism of the mastication of rubber. VIII. The reaction of natural rubber with 3,5-dibromobenzoyl peroxide 808

JORCZAK, J. S. See FETTES, E. M.
JUVE, A. E. See BEATTY, J. R.
———, AND BEATTY, J. R. Shrinkage of mold-cured elastomer compositions 1141

KAINRADL, P., AND HÄNDLER, F. Heat build-up and destruction of vulcanizates under dynamic stress 153
KARPOVICH, V. I., AND LUKIN, B. V. X-Ray investigation of the amorphous state of rubber 728

Page

KELLÖ, V. See TKÁČ, A.
———, AND TKÁČ, A. Reaction kinetics in the aging of natural rubber by infrared spectrography. III. Effect of light and antioxidants 968
KIRIYAMA, SHIGERU. See IMOTO, MINORU.
KLITENIK, G. S. See GUL, V. E.
KONEKOV, K. S. See BARTENEV, G. M.
KOVACIC, PETER. Bisalkylation theory of Neoprene vulcanization 1021
———. See ANDERSEN, D. E.
KÜNZLE, OTHMAR. See KUHN, WERNER.
KUHN, WERNER, AND KÜNZLE, OTHMAR. Experimental determination of the dynamic viscosity and elasticity and also of the relaxation time spectrum of rubber ... 694
KUZMINSKIĬ, A. S. See REITLINGER, S. A.
———, AND BASS, I. Joint influence of free and combined sulfur and *N*-phenyl-2-naphthylamine on the oxidation of vulcanized rubber 793
———, AND CHERTKOVA, V. F. Role of oxygen in the vulcanization of natural rubber 785
———, AND LEZHNEV, N. N. Inhibited oxidation of elastomers 412
——, MAIZELS, M. G., AND LEZHNEV, N. N. Mechanical activation of the initation of oxidation of elastomers 429

LEZHNEV, N. N. See KUZMINSKIĬ, A. S.
LUKIN, B. V. See KARPOTOCHKIN, V. I.
LUKOMSKAYA, A. I., AND DOGADKIN, B. A. Structure and properties of loaded rubber mixtures. XII. Dielectric properties of natural rubber-carbon black mixtures ... 84
LYONS, J. A. See FARMER, E. H.

MAASSEN, G. C. See YOUMANS, R. A.
MCCAFFREY, F. See HONNOLD, V. R.
MCLEOD, L. A. See HENDERSON, D. A.
MCSWEENEY, G. P. See BRADEN, M.
MADGE, E. W., COLLIER, N. M., AND NEWNHAM, J. L. M. Zinc oxide testing of latex 1211
MAIZELS, M. G. See KUZMINSKIĬ, A. S.
MANDELKERN, LEO. See ROBERTS, DONALD E.
MARSHALL, D. G., WALKER, D. L., AND SMITH, J. G. Softening of vulcanized black-loaded rubber during extension 1123
MARTIN, B. J. A., AND PARKINSON, D. Milling procedure: its effect on physical properties 261
MAZEL, M. I. See ERMOLENKO, I. N.
MERRETT, F. M. Interaction of polymerizing systems with rubber and its homologs. II. Interaction of rubber in the polymerization of methyl methacrylate and of styrene 72
MOONEY, M., AND WOLSTENHOLME, W. E. The rheological unit in raw elastomers ... 488
MOORE, C. G., AND SAVILLE, R. W. Reactions of amines and sulfur with olefins. I. The reaction of diethylamine and sulfur with cyclohexene 92
II. The reaction of diethylamine and sulfur with cyclohexene 102
MORRELL, S. H. See BENT, L. L.
MORRISSEY, R. T. Butyl type polymers containing bromine 952
MORTON, MAURICE. Molecular weights of emulsion polydienes 732
MROWCA, B. A. See HONNOLD, V. R.
MULLINS, L. See GUMBRELL, S. M.

NEWNHAM, J. L. M. See MADGE, E. W.
NISONOFF, ALFRED. See HOWLAND, L. H.
NOLLE, A. W. See HUTTON, ALLEN Q.
NOVIKOV, A., AND GALIL-OGLY, F. A. Effect of structurizing agents on the plasticization and vulcanization of butadiene-styrene rubber 57
NOVIKOVA, N. M. See BARTENEV, G. M.
NYBURG, S. C. X-Ray determination of crystallinity in deformed natural rubber. 999

Page

Oberto, Stefano. New instruments for measuring hardness 1054
Ossefort, Z. T., and Touhey, W. J. Ozone crazing of biaxially stressed GR-S vulcanizates 1119

Pande, J. B. See Ramakrishnan, C. S.
Panek, J. R. See Fettes, E. M.
Parienté, Claude. Study of some heat-sensitizing agents of Hevea latex 1166
Parkinson, D. See Martin, B. J. A.
Paton, F. J. Significance of the yellow fraction in spontaneous coagulation 1204
Pinazzi, C. P., and Billuart (Mrs.) M. Protection of natural rubber. I. The effects of nickel dibutyldithiocarbamate alone and in combination with protective agents 438
Polley, M. H. See Chappuis, M. M.
Priss, L. S. See Reznikovskiĭ, M. M.

Raghunath, D. See Ramakrishnan, C. S.
Ramakrishnan, C. S., Raghunath, D., and Pande, J. G. Chlorination of natural rubber solutions by means of phenyl iododichloride 598
Ratner, S. B. See Babtenev, G. M.
Reitlinger, S. A., and Kuzminskiĭ, A. S. Solubility of *N*-phenyl-2-naphthylamine in elastomers 186
Resing, W. L. See Gils, G. E. van.
Reznikovskiĭ, M. M., Priss, L. S., and Dogadkin, B. A. Study of the laws of deformation of loaded elastomers 684
Rivlin, R. S. See Gumbrell, S. M.
Roberts, Donald E., and Mandelkern, Leo. Nature of stark rubber 1007
———. Thermodynamics of crystallisation in high polymers. Natural rubber 718
Roelig, Hermann, and Fromandi, Guido. Determination of the resistance of soft-rubber parts to periodic stressing, and its relationship to energy absorption and deformation 1044
Roth, Frank L., Decker, George E., and Stiehler, Robert D. Temperature control during mixing of rubber compounds 1157

Salomon, G., and Scheé, Chr. van der. Infrared analysis of isomerized, vulcanized, and oxidized natural rubber 213
———. Infrared analysis of some chlorinated natural rubbers 224
Sandomirskiĭ, D. M., and Gagina, K. Formation of rubber films from solutions and aqueous dispersions 527
Saville, R. W. See Glazebrook, R. W.; Moore, C. G.
Sazonova, L. P. See Blokh, G. A.
Schallamach, A. Abrasion of rubber 906
Scheé, Chr. van der. See Salomon, G.
Schonlau, W. J. K. Migration of antioxidants during oven aging 379
Schreuer, E. Softness, impact time, and internal damping of technical rubber mixtures 145
Schulman, J. H. See Glazer, J.
Schuls, R. A. See Chappuis, M. M.

Page

Scott, J. R. Rubber hardness testing 1071
Smallwood, Hugh M. See Barton, Bernard C.
Smith, G. E. P. Jr. See Amberlano, J. C.; Bennett, R. C.
Smith, J. G. See Marshall, D. G.
Stalinsky, Eugène. Energy consumed in the plasticization of rubber on a roll mill . 606
———. The plasticization of rubber on roll mills. A correction 573
Starobinets, G. L., and Aleksandrovich, Kh. M. Thermodynamics of the swelling of natural rubber and sodium-butadiene rubber in binary mixtures 838
Stiehler, Robert D. See Roth, Frank L.
Storey, E. B. See Edwards, D. C.

Talalay, Joseph A. Load-carrying capacity of latex foam rubber 358
Taylor, James S. See Crampsey, Edward; Gordon, Manfred.
Tempel, M. van den. Solubility of zinc oxide in preserved Hevea latex 927
———. See Vries, A. J. de.
Thorsrud, A. Influence of salt coagulants on the properties and on the aging of products made by the dipping process 1175
Tkáč, A. See Kelló, V.
———, and Kelló, V. Study by infrared spectrography of the aging of natural rubber. II. Effect of light (Experimental results) ..... III, 383, 968
———, and Hrivíkova, J. Reaction kinetics in the aging of natural rubber by infrared spectrography. IV. Effect of the wave length of the radiation and the temperature on aging by light 986
Touhey, W. J. See Ossefort, Z. T.
Tunnicliffe, M. E. Nonrubber components of ammonia-preserved latex. An analytical study 673

Vries, A. J. de, and Tempel, M. van den. Structure and rheological properties of Hevea latex gels 922

Walker, D. L. Pressure coefficient of resistance of conductive rubber 519
———. See Marshall, D. G.
Watson, W. F. Combination of rubber and carbon black on cold milling 1032
Weidner, V. See Ebert, G.
Wilkinson, C. S. Jr. See Gehman, S. D.
Wolstenholme, W. E. See Mooney, M.
Wood, Lawrence A. Crystallization in butadiene-styrene copolymers 51
———. Mooney viscosity changes in freshly prepared raw natural rubber 917
Woodford, R. See Field, J. E.
Wratten, R. See Bulgin, D.
Wynne-Evans, C. Determination of free sulfur in hard rubber 1221

Youmans, R. A., and Maassen, G. C. Correlation of room temperature shelf aging with accelerated aging 1133

Zuev, Y. S. Protection of rubbers against ozone cracking 788

SUBJECT INDEX

Abrasion
of rubber 906
and slippage 1082
Accelerated aging 1133
Accelerated coagulation of latex 1193
Acids, water-soluble, of latex 657
Activation, mechanical, of initiation oxidation 429
Aging
by light 989
of natural rubber
reaction kinetics in 968, 989
study by infrared spectrography of 383
of products made by dipping process 1175
of pure-gum rubber mixtures 420
shelf, with accelerated aging 1133
stability of Neoprene latex 628
and weathering of rubber 230
Allylic chlorine, hydrolysis of 628
Amines, reactions of, with olefins 92, 102, 109
Amorphous state of rubber 728
Analysis, infrared 213, 224
Antioxidants, effect of light and 968

Behavior of reclaiming agents in sulfur and nonsulfur GR-S vulcanizates 322

Page

Benzoyl peroxide, curing silicone rubber with . 865
Biaxially stressed GR-S vulcanizates 1119
Binary mixtures, swelling in 828
Bisalkylation theory of Neoprene vulcanization 1021
Breakage of rubber-filler linkages and energy dissipation in stressed rubber 540
Bromine in Butyl type polymers 952
Buna-N rubber 131
Butadiene-styrene
copolymers 121, 557
rubber 57
Butyl
type polymers containing bromine 952
vulcanizates 1096

Carbon black
compounds 570
dielectric properties 891
dispersion 202
mixtures 84
performance of mixtures of 878
promoters for reaction of rubber with 895
and rubber 1032
Carboxylic elastomers 937
Changes in elastomers due to radiation from cobalt^{60} 12
Chemistry in carbon black dispersion 202
Chlorinated natural rubbers 224
Chlorination of natural rubber solutions 598
Coagulants, salt 1175
Coagulation,
accelerated, of latex 1193
spontaneous 1204
sulfuric acid 1185
Cobalt^{60} 12
Combination of rubber and carbon black on cold milling 1032
Conductive rubber, resistance of 519
Copolymers, microstructures of 121
Correlation of room-temperature shelf aging with accelerated aging 1133
Cracking, ozone 788
Crazing, ozone, of GR-S vulcanizates 1119
Cream in GR-S latex 641
Crepe rubber, vulcanization by sulfur monochloride 278
Crystallinity, x-ray determination of 999
Crystallization
in butadiene-styrene copolymers 51
in natural rubber. II 457
III 460
and relaxation of stress in stretched natural-rubber vulcanizates 36
thermodynamics of, in high polymers 718
Cross-linking
of allylic chlorine 628
of rubber by pile radiation 1
Curing of silicone rubber with benzoyl peroxide 865
Cyclohexane, reaction of diethylamine and sulfur with 92

Damping, internal 145
Deformation and energy absorption 1044
Deformed natural rubber, crystallinity in 999
Degradation of high polymers. Scission reactions in oxidation of GR-S. I 746
II 758
Departures of the elastic behavior of rubbers in simple extension from the kinetic theory 24
Destruction of vulcanizates under dynamic stress 153
Determination
of free sulfur in hard rubber 1221
of resistance of soft-rubber parts to periodic stressing, and its relationship to energy absorption and deformation 1044
3,5-Dibromobenzoyl peroxide, reaction with natural rubber 808
Dielectric
loss measurements 420
properties of natural rubber-carbon black mixtures 84
properties of rubber mixtures containing carbon black 891

Page

Diethylamine, reaction of,
with 1,5-diolefins 109
and sulfur 92
with trialkylethylene 102
Dilatometric method of vulcanization of crepe rubber 850
Dipping process 1175
Dispersions
aqueous, rubber films from 527
carbon black 202
Dynamic
modulus of a Buna-N rubber 131
stress and heat build-up of vulcanizates 153
viscosity of rubber 694

Effect
of fillers on permeability of rubber to gases . 821
of molecular interaction on the light scattering of rubber solutions 494
of structurizing agents on the plasticization and vulcanization of butadiene-styrene rubber 57
of sulfuric acid coagulation on properties of natural rubber 1185
Elastic behavior, departures from 24
Elasticity
measurement of loss of 711
of rubber 694
Electron microscope 253
Electron-microscopic study of the locus of a latex reaction 623
Elongation and relaxation of rubber 675
Emulsion polydienes, molecular weights of ... 732
Energy
absorption and deformation 1044
consumed in the plasticization of rubber on a roll mill 606
dissipation of rubber-filler linkages 540
Evidence for a hydrochlorination retarder within natural-rubber latex particles 918
Experimental
determination of the dynamic viscosity and elasticity and also of the relaxation time spectrum of rubber 964
study of low-frequency effects on the dynamic modulus of a Buna-N rubber .. 131
Extension
simple, departures of elastic behavior in 24
softening during 1123

Fillers
effect of, on permeability to gases 821
reinforcing rubber 506
rubber-, linkages 540
Films from solutions 527
Flow characteristics of rubber 534
Formation of rubber films from solutions and aqueous dispersions 527
Fraction, high-molecular, of rubber hydrocarbon 504
Free
-radical activity of reinforcing rubber fillers 506
sulfur in hard rubber 1221

Gases, effect of fillers on permeability to gases 821
Gelation method 278
GR-S
latex, formation of cream in 641
reclaiming agents 308
vulcanizates 322
ozone crazing of 1119

Hard rubber, free sulfur in 1221
Hardness
new instruments for measuring 1054
testing of rubber 1071
Heat
build-up and destruction of vulcanizates under dynamic stress 153
sensitizing agents 1166
Homologs of rubber 72
Hydrocarbon, high-molecular fraction 504
Hydrochlorination
of latex 288
retarder in latex particles 918
of rubber 297

Page

Hydrogen sulfide-sulfur dioxide, sulfuration of trialkylethylenes with ... 470
Hydrolysis of allylic chlorine ... 628

Impact time of technical rubber mixtures ... 145
Importance of the polar component of mixed fluids in the swelling of vulcanizates ... 833
Impurities, influence of, in crystallization of rubber ... 457
Influence of salt coagulants on the properties and on the aging of products made by the dipping process ... 1175
Infrared
  analysis
    of some chlorinated natural rubbers ... 224
    of isomerized, vulcanized, and oxidized natural rubber ... 213
  spectrography ... 968, 989
  of aging natural rubber, study by ... 383
  study of oxidation of elastomers ... 770
Inhibited oxidation of elastomers ... 412
Instruments, new, for measuring hardness ... 1054
Interaction
  of polymerizing systems with rubber and its homologs. II. Interaction of rubber in the polymerization of methyl acrylate and of styrene ... 72
  of sulfur and sulfur compounds with olefinic substances. VII. Low-temperature sulfuration of trialkylethylenes with hydrogen sulfide-sulfur dioxide and with a sulfur-zinc dithiocarbamate system ... 470
Introduction to the mechanism of the hydrochlorination of rubber ... 297
Isomerized natural rubber, infrared analysis of ... 213

Joint influence of free and combined sulfur and *N*-phenyl-2-naphthylamine on the oxidation of vulcanized rubber ... 793

Kinetic study
  study of oxidation of GR-8 in solution ... 746
  theory, departures of elastic behavior from ... 24
Kinetics
  and mechanism of hydrochlorination of synthetic and natural polyisoprene latex ... 288
  reaction in aging by infrared spectrography ... 383, 968

Latex
  accelerated coagulation of ... 1193
  ammonia-preserved ... 673
  GR-8, formation of cream in ... 641
  Hevea
    heat sensitizing agents of ... 1166
    water-soluble acids of ... 657
    zinc oxide in ... 927
  Neoprene, aging stability of ... 628
  non-rubber components of ... 673
  particles, hydrochlorination retarder in ... 918
  polyisoprene ... 218
  reaction locus of ... 623
  zinc oxide testing of ... 1211
  gels, rheological properties of ... 922
  of deformation of loaded elastomers ... 684
  of unidimensional compression and stretching of rubber ... 19
Light
  aging by ... 989
  effect
    of antioxidants and ... 968
    of, on study by infrared spectrography ... 383
  scattering of rubber solutions ... 494
Load-carrying capacity of latex foam rubber ... 358
Loaded
  elastomers, laws of deformation of ... 684
  rubber mixtures ... 84
Low-frequency effects of Buna-N rubber, study of ... 131
Low-temperature
  properties of plasticized butadiene-styrene copolymers ... 557
  stability of rubber ... 711
  testing elastomers at ... 335

Page

Magnetism, nuclear, studies by ... 480
Mastication of rubber, mechanism of ... 808
Measurements of steady flow characteristics of rubber at high rates of shear ... 534
Mechanical
  activation of the initiation of oxidation of elastomers ... 429
  properties of high polymers, representation by the model method ... 66
Mechanism
  of formation of cream in GR-8 latex ... 641
  of hydrochlorination
    of latex ... 288
    of rubber ... 297
  of vulcanization of polysulfide rubbers ... 139
Methyl methacrylate, polymerization of ... 72
Microscope, electron ... 253
Microscopic, electron- study of locus of latex reaction ... 623
Microstructures of polybutadienes and butadiene-styrene copolymers ... 121
Migration of antioxidants during oven aging ... 379
Milling
  cold ... 1032
  procedure: its effect on physical properties ... 261
Mixing, temperature control during ... 1157
Mixtures of natural rubber and other elastomers ... 814
Model method, representation of mechanical properties by ... 66
Modulus, dynamic, of a Buna-N rubber ... 141
Mold-cured elastomer compositions ... 1141
Molecular weight
  of emulsion polydienes ... 732
  osmotic measurements ... 504
Mooney
  viscometer ... 588
  viscosity changes in freshly prepared raw natural rubber ... 917

Nature of stark rubber ... 1007
Neoprene
  latex, aging stability of ... 628
  vulcanization ... 1021
New instruments for measuring hardness ... 1054
N-phenyl-2-naphthylamine
  in elastomers ... 186
  influence of oxidation ... 793
Nickel dibutyldithiocarbamate, effects of ... 438
Nonrubber components of ammonia-preserved latex. An analytical study ... 673
Nonsulfur GR-8 vulcanizates ... 322
Nuclear magnetism, studies by ... 480

Olefinic substances, interaction of sulfur with ... 470
Olefins, reactions of amines with ... 92
Osmotic measurements of molecular weight ... 504
Oxidation
  of elastomers ... 429
    infrared study of ... 770
    inhibited ... 412
  of GR-8 in solution ... 746
  of vulcanized rubber ... 793
Oxidized natural rubber, infrared analysis of ... 213
Oxygen
  relation of, to GR-8 reclaiming agents ... 308
  role of, in vulcanization of natural rubber ... 785
Ozone
  in air, low concentrations of ... 608
  crazing of biaxially stressed GR-8 vulcanizates ... 1119
  resistance of Butyl vulcanizates ... 1096

Performance of carbon blacks. Influence of surface roughness and porosity ... 878
Permeability to gases ... 814, 821
Peroxides, organic, vulcanization by ... 190
Phenyl iodochloride ... 598
Physical properties, effect of milling procedure on ... 261
Pile radiation, cross-linking of rubber in ... 1
Plasticization
  of rubber on roll mills ... 606, 673
  and vulcanization of butadiene-styrene rubber ... 57

Page

Plasticized butadiene-styrene copolymers.... 557
Polar component of mixed fluids..... 833
Polybutadienes, microstructures of..... 121
Polydienes, molecular weights of emulsion... 732
Polyisoprene latex..... 288
Polymerizing systems, interaction of, with rubber..... 72
Polysulfide rubbers, mechanism of vulcanization of..... 139
Porosity of carbon blacks..... 878
Pressure coefficient of resistance of conductive rubber..... 519
Promoters for the reaction of rubber with carbon black..... 895
Protection
of natural rubber. I. The effects of nickel dibutyldithiocarbamate alone and in combination with protective agents... 438
of rubbers against ozone cracking..... 788
Protective agents with nickel dibutyldithiocarbamate..... 438
Pure-gum
compounds, vulcanizing variability of rubber in..... 570
rubber mixtures, aging of..... 420

Radiation
cobalt^{60}, changes due to..... 12
effect of wave length of..... 989
pile..... 1
Raw elastomers, rheological unit in..... 488
Reaction
kinetics in the aging of natural rubber by infrared spectrography
II. 383
III. Effect of light and antioxidants.... 968
IV. Effect of the wave length of the radiation and the temperature on aging by light..... 989
of a thiuram with sulfur..... 804
Reactions of amines and sulfur with olefins.
I. The reaction of diethylamine and sulfur with cyclohexene..... 92
II. The reaction of diethylamine and sulfur with trialkylethylenes..... 102
III. The reaction of diethylamine and sulfur with 1,5-diolefins..... 109
Reclaiming agents
in GR-S..... 308
in vulcanizates..... 322
Reinforced rubber stocks under the electron microscope..... 253
Reinforcing rubber fillers..... 596
Rheological unit in raw elastomers..... 488
Relation of oxygen to the activity of GR-S reclaiming agents..... 398
Relaxation
of rubber, thermal effect in..... 675
time spectrum of rubber..... 694
of stress in stretched vulcanizates..... 36
Representation of the mechanical properties of high-polymers by the model method... 66
Role of oxygen in the vulcanization of natural rubber..... 785
Rubber hardness testing..... 1071

Shrinkage of mold-cured elastomer compositions..... 1141
Significance of the yellow fraction in spontaneous coagulation..... 1204
Simple objective method for estimating low concentrations of ozone in air..... 608
Slippage and abrasion..... 1082
Smearing of vulcanized rubber..... 508
Softening of vulcanized black-loaded rubber during extension..... 1123
Softness, impact time, and internal damping of technical rubber mixtures..... 145
Solubility
of *N*-phenyl-2-naphthylamine in elastomers 186
of zinc oxide in preserved Hevea latex..... 927
Some osmotic measurements of the molecular weight of a high-molecular fraction of rubber hydrocarbon..... 504
Stark rubber..... 1007
Stressing, periodic..... 1044
Structure
and dielectric properties of rubber mixtures containing carbon black..... 891
and properties of loaded rubber mixtures. XII. Dielectric properties of natural rubber-carbon black mixtures..... 84
and rheological properties of Hevea latex gels..... 922
Studies of the mechanism of the mastication of rubber. VIII. The reaction of natural rubber with 3,5-dibromobenzoyl peroxide 808
Studies of rubberlike polymers by nuclear magnetism..... 480
Study
by infrared spectrography of the aging of natural rubber. II. Effect of light (Experimental results)..... 383
of the laws of deformation of loaded elastomers..... 684
of permeability to gases. Mixtures of natural rubber and other elastomers..... 814
of some heat-sensitizing agents of Hevea latex..... 1166
Sulfur, free..... 1221
Sulfuric acid coagulation..... 1185

Temperature control during mixing of rubber compounds..... 1157
Test of the applicability of dielectric loss measurements to the study of the aging of pure-gum rubber mixtures..... 420
Testing of rubber for its low-temperature stability by measurement of the loss of elasticity..... 711
Thermal effect in the elongation and relaxation of rubber..... 675
Thermodynamics
of crystallization in high polymers. Natural rubber..... 718
of swelling of natural rubber and sodium-butadiene rubber in binary mixtures..... 838

Vulcanization
of rubber by organic peroxides..... 190
of crepe rubber by sulfur monochloride
I. The gelation method..... 278
II. The dilatometric method..... 850
Vulcanizing variability of natural rubber in pure-gum and carbon black compounds.. 570

Water-soluble acids of the latex of Hevea brasiliensis..... 657

x-Ray
determination of crystallinity in deformed natural rubber..... 999
investigation of the amorphous state of rubber..... 728

Zinc oxide testing of latex..... 1211

THE VANDERBILT LABORATORY

...Located in East Norwalk, Connecticut. Maintained as a development and technical service center in the interest of our customers and their efficient use of Vanderbilt materials for Dry Rubber, Latex, and Plastics Compounding.

Products of Vanderbilt Research it Will Pay You to Investigate...

BISMATE
in rubber or GR-S–rubber blends

CUMATE
in GR-S

TELLURAC
in Butyl

...Practical and powerful dithiocarbamate ultra accelerators for faster curing compounds.

R. T. VANDERBILT CO., INC.
230 Park Avenue, New York 17, N. Y.

News about

B. F. Goodrich Chemical *raw materials*

Good-rite Resin 50

improves processing

Good-rite Resin 50—a thermoplastic reinforcing resin that is compatible with crude and American rubbers—offers the compounder many important advantages.

- ★ **Improves mixing, calendering, and extrusion characteristics of compounds to which it is added.**
- ★ **Easily handled; does not require masterbatching.**
- ★ **Makes premium quality compounds in all ranges of hardness.**
- ★ **Makes easy-to-extrude high-hardness compounds in full range of colors.**

Good-rite Resin 50 is produced as a finely divided, free-flowing, odorless white powder, easily blended with other polymers. To find out how Resin 50 will enable you to make *better* products at *lower costs*, please write Dept. CK-4, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio. In Canada: Kitchener, Ontario. Cable address: Goodchemco.

makes premium products

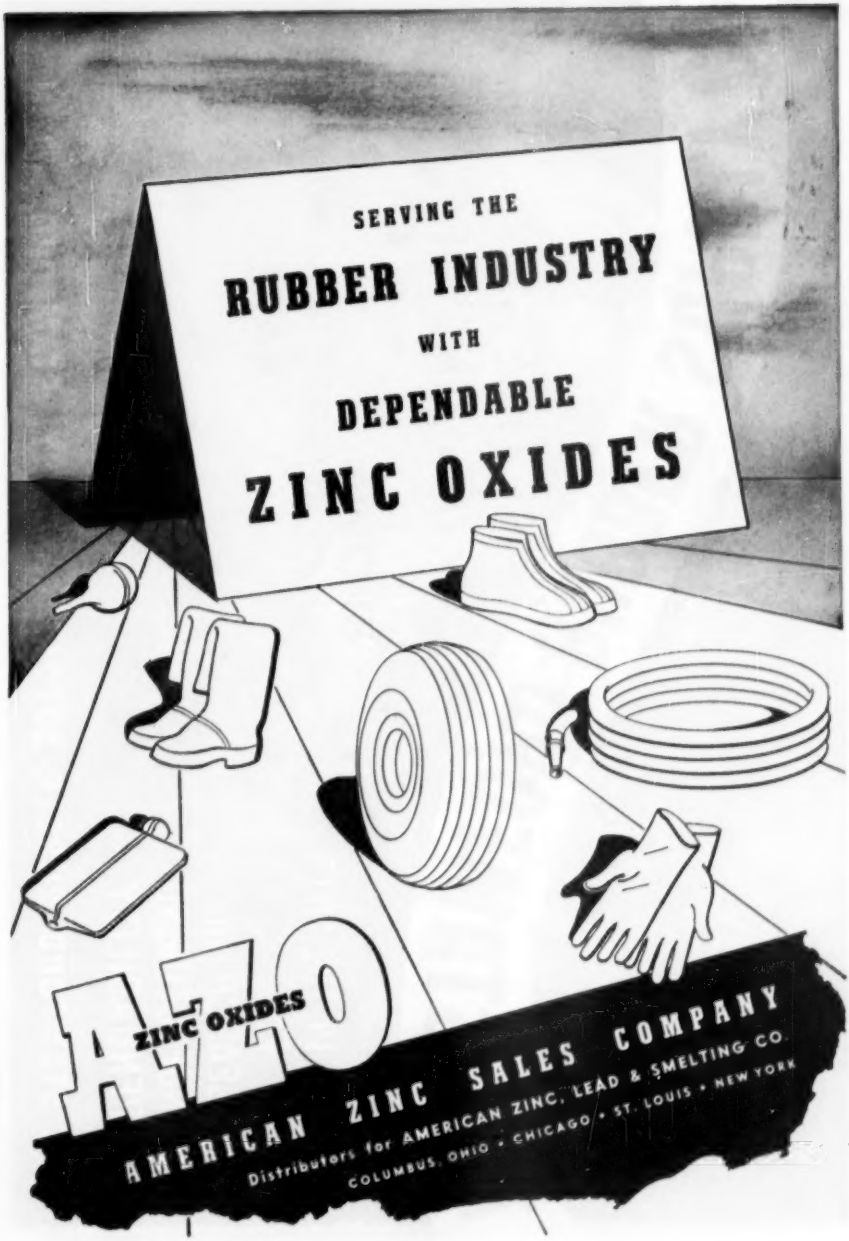
You'll find Resin 50 in the recipe wherever the product needs superior flex life, hardness without sacrifice of strength, improved abrasion resistance, and light weight. Are any of your products listed here?

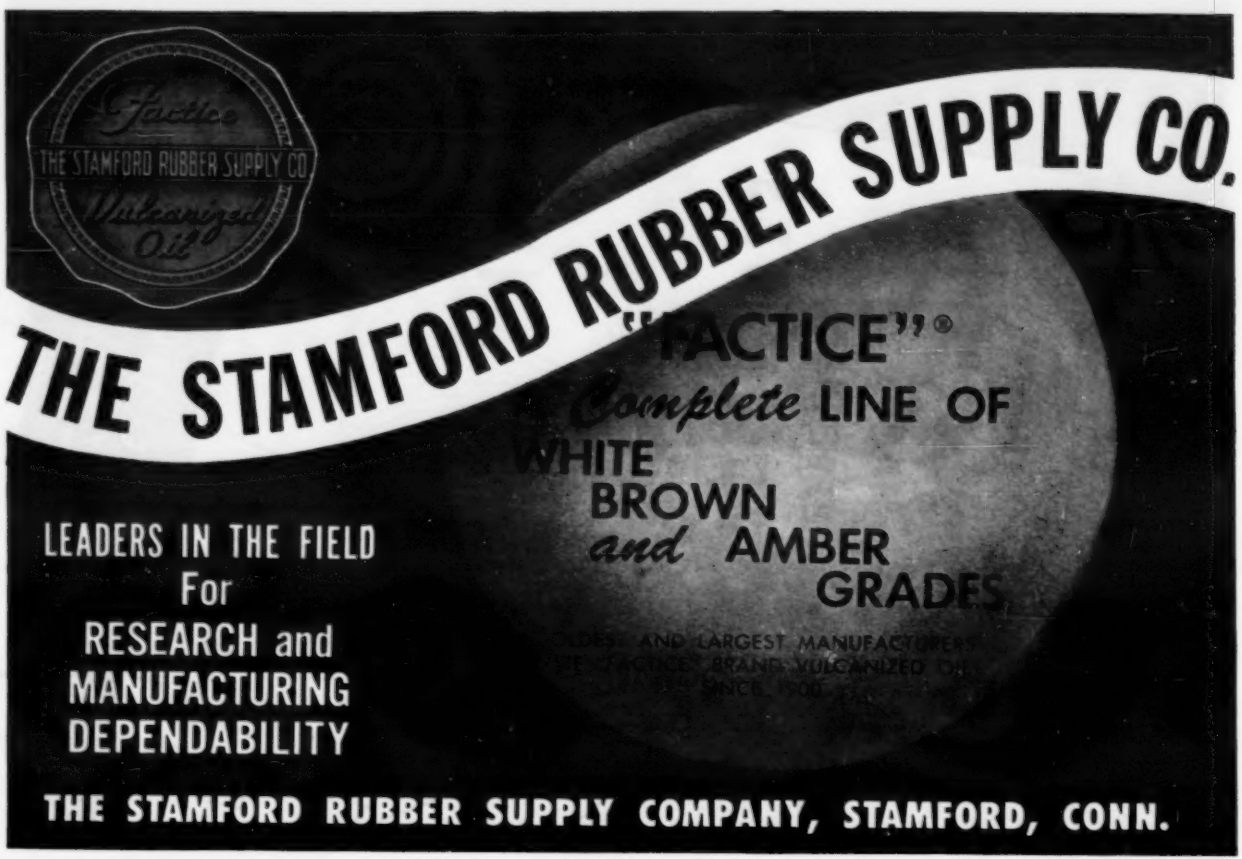
- ★ **Floor Tile, Under-chair Pads**
- ★ **Shoe Soles, Safety Shoes**
- ★ **Golf Bag Bottoms, Club-heads**
- ★ **Wire & Cable Insulation**
- ★ **Battery Cases, Battery Caps**
- ★ **Drainboards, Strainers**

B. F. Goodrich Chemical Company
A Division of The B. F. Goodrich Company

Hycar American Rubber

GEON polyvinyl materials • HYCAR American rubber and latex • GOOD-RITE chemicals and plasticizers • HARMON colors


SERVING THE
RUBBER INDUSTRY
WITH
DEPENDABLE
ZINC OXIDES
AZO
ZINC OXIDES
AMERICAN ZINC SALES COMPANY
Distributors for AMERICAN ZINC, LEAD & SMELTING CO.
COLUMBUS, OHIO • CHICAGO • ST. LOUIS • NEW YORK


Factice
THE STAMFORD RUBBER SUPPLY CO
Vulcanized Oil
THE STAMFORD RUBBER SUPPLY CO.
"FACTICE"®
Complete LINE OF
WHITE
BROWN
and AMBER
GRADES
LEADERS IN THE FIELD
For
RESEARCH and
MANUFACTURING
DEPENDABILITY
THE STAMFORD RUBBER SUPPLY COMPANY, STAMFORD, CONN.

DON'T BE AN Old Fashioned COMPOUNDER

...Get Hep to

STABILITE*

ANTIOXIDANT

*Manufactured by Chemico, Inc.
Distributed by The C. P. Hall Co.

AKRON, OHIO
LOS ANGELES, CALIF.
CHICAGO, ILLINOIS
NEWARK, N. J.

The C. P. Hall Co.
CHEMICAL MANUFACTURERS

VULCANOL®

Latex Compounds of Proven Quality

VULCACURE®

AQUEOUS SUSPENSIONS OF ULTRA ACCELERATORS

ALCOGUM

Sodium Polyacrylate Latex Thickener and Stabilizer

VULCARITE®

A Series of Water Dispersions of Latex Compounding Chemicals

•

Technical information and samples forwarded promptly upon request.

ALCO OIL & CHEMICAL CORP.

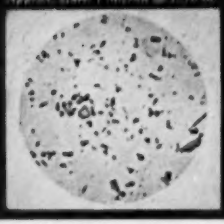
TRENTON AVE. AND WILLIAM ST., PHILADELPHIA 34, PA.

WEST COAST REPRESENTATIVE:
H. M. Royal, Inc.
Whse., 4814 Loma Vista Ave.,
Los Angeles 58, Calif.

NEW ENGLAND OFFICE
Alco Oil & Chemical Corp.
610 Industrial Trust Bldg.
111 Westminster St.,
Providence 3, R. I.

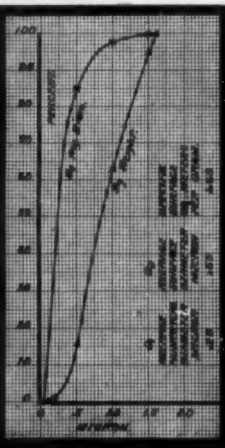
for high quality

RUBBER PRODUCTS



ST. JOE GREEN LABEL #42

Representative Chemical Tests	
ZnO	99.20%
Pb	.03
Cd	.01
Mn	.003
Cu	.002
Acidity as SO_3	.03
Total S as SO_3	.05
H_2O soluble salts	.15
Insoluble in HCl	.15
Loss at 110° C.	.30
Representative Physical Tests	
Particle size	
Average numerical diameter D_1 —microns	.28
Average surface diameter D —microns	.65
Specific surface—Sq.M./gram	1.69
Percent fines under .50 micron	16.0
Specific gravity	5.65
Apparent density—lb./cu. ft.	30.
Cleanliness	
Percent thru 325 mesh screen	99.97



Particle Size Distribution

ST. JOSEPH LEAD COMPANY

250 PARK AVE.
NEW YORK CITY 17

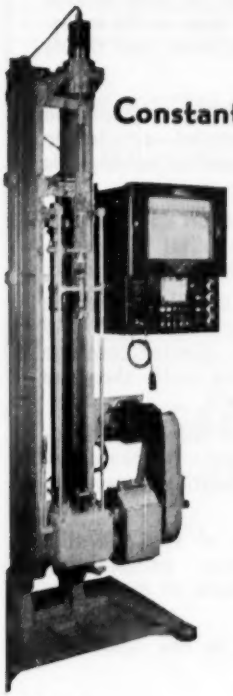
Plant & Laboratory: Monaca (Josephtown) Pa.

In the group of St. Joe fast curing zinc oxides, **Green Label #42** has long been preferred by many manufacturers of high quality rubber products. Some of the reasons for this preference — in addition to its excellent activating and reinforcing properties — are its rapid incorporation into rubber, combined with ease and completeness of dispersion.

Complete physical and chemical properties of St. Joe rubber grade zinc oxides are described in our new technical manual, ST. JOE ZINC OXIDES. Write for your free copy—on your company letterhead please.

NOW FOR THE FIRST TIME

A PRECISION tester capable of recording all of your tensile results in POUNDS PER SQUARE INCH or equivalent units.



SCOTT TESTERS *
"ACCR-O-METER"

Constant-Rate-of-Extension Weighing System

An ingenious electrical circuit permits compensation for differences in area of test specimens reducing results to a common denominator—any selected P.S.I.

WHAT ARE YOUR PROBLEMS?

Rubber

—standard dumbell specimens varying in thickness.

—tubing or insulated wire jackets varying in O.D. & I.D.

—thread varying in square mils.

Wire

—copper, tungsten, silver, etc. varying in diameter.

Metal

—sheet or strip varying in thickness or width.

Textile

—yarns varying in tensile.

Any specimen of any material with measurable area.

With the completely flexible Accr-O-meter providing infinitely variable loads from 0.1# up to 2000#, and the equation

PSI = LOAD/AREA

any or all of the above are readily attainable.

Request Details

SCOTT TESTERS, INC. 102 Blackstone St. Providence, R. I.

Scott Testers — Standard of the World

* Trademark

All dolled up.....
and goes everywhere

In keeping with today's publishing trends, Rubber World has changed its physical appearance, to offer readers a fresh, modern look and an easy to read format—yet a magazine backed by more than 65 years of valued experience. From cover to cover Rubber World is a publication devoted to the technical man in the industry, and is designed for quick reading of its accurate and timely technical material.

RUBBER WORLD has NOT changed

its leadership in publishing original and accurate technical material—articles to help the production man in solving his many problems.

its policy of maintaining an Editorial Advisory Board, to aid the Editor in presenting completely accurate facts and data.

its circulation policy of complete coverage of the rubber industry. Rubber World now offers almost 25% greater coverage of rubber manufacturing staffs than the nearest paper in the field.

its policy of offering an AUDITED circulation, more than 65% paid, in accordance with U. S. Postal Regulations governing 2nd Class mail.

its complete coverage of the scientific and technical activities, personalities, meetings, and other items of interest to readers.

its position of respect in the rubber industry.

For complete details of its service to the industry write

RUBBER WORLD

386 FOURTH AVENUE NEW YORK 16, N. Y.

ANTIMONY SULPHIDE

Regular Grades *for* Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

RARE METAL PRODUCTS CO. **ATGLEN, PENNA.**

SUPERIOR ZINC CORPORATION

121 North Broad Street **Philadelphia 7, Penna.**

Works at Bristol, Pa.

VULCANIZED VEGETABLE OILS

• RUBBER SUBSTITUTES •

THE CARTER BELL MFG. CO. SINCE CARTER BELL PRODUCTS 1903 SPRINGFIELD, NEW JERSEY

REPRESENTED BY

HARWICK STANDARD CHEMICAL CO.

Akron — Boston — Trenton — Chicago — Denver — Los Angeles

WHITETEX

A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA

A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO

For compounding rubber and synthetic rubber.

No. 33 CLAY

For wire and vinyl compounding.

●

For full details, write our Technical Service Dept.

SOUTHERN CLAYS, INC.

(Formerly P. W. Martin Gordon Clays, Inc.)

33 Rector Street · New York 6, N.Y.

CARBON BLACKS

Wyex (EPC)
Easy Processing Channel Black

Arrow TX (MPC)
Medium Processing Channel Black

Essex (SRF)
Semi-Reinforcing Furnace Black

Modulex (HMF)
High Modulus Furnace Black

Aromex HAF
High Abrasion Furnace Black

Arogen GPF
General Purpose Furnace Black

Aromex CF
Conductive Furnace Black

Aromex ISAF Intermediate
Super Abrasion Furnace Black

Aromex SAF
Super Abrasion Furnace Black

Arovel (FEF)
Fast Extruding Furnace Black

Collocarb
80% Carbon Black + 20% Process Oil

CLAYS

Suprex Clay . . . . High Reinforcement
Paragon Clay . . . . . Easy Processing
Hi-White R . . . . . White Color

RUBBER CHEMICALS

Turgum S, Natac, Butac . . . . . Resin-Acid Softeners
Aktone . . . . . Accelerator Activator
Zeolex 23 . . . . . Reinforcing White Pigment

HUBER **J. M. HUBER CORPORATION** · 100 Park Ave., New York 17, New York

consult **TITANOX** *technical service department*

for assistance with your white pigmentation problems

1660

TITANIUM PIGMENT CORPORATION

Subsidiary of NATIONAL LEAD COMPANY

TITANOX
the brightest name in pigments

RUBBER CHEMISTRY AND TECHNOLOGY IS SUPPORTED BY ADVERTISING FROM THESE LEADING SUPPLIERS

INDEX TO ADVERTISERS

	Page
Alco Oil and Chemical Corporation	23
American Cyanamid Company, Organic Chemicals Division	12
American Zinc Sales Company	21
Cabot, Godfrey L., Inc.	11
Carter Bell Manufacturing Company, The	27
Columbian Carbon Company (opposite Table of Contents)	18
Du Pont, Elastomers Division (Chemicals)	7
Du Pont, Elastomers Division (HYPALON)	32
Goodrich, B. F., Chemical Company	20
Goodyear, Chemical Division	4
Goodyear, Chemical Division	5
Hall, C. P. Company, The	23
Harwick Standard Chemical Company	(Inside Back Cover)
Huber, J. M., Corporation	29
Koppers Company, Inc. (Chemical Division)	13
Monsanto Chemical Company	9
Naugatuck Chemical Division (U.S. Rubber Company)	15
Neville Chemical Company	14
New Jersey Zinc Company, The	(Outside Back Cover)
Pan American Refining Corporation, Pan American Chemicals Division	10
Phillips Chemical Company	(Opposite Inside Front Cover) 1
Rare Metal Products Company	27
Richardson, Sid, Carbon Company	8
Rubber Age, The	31
Rubber World	26
St. Joseph Lead Company	24
Scott Testers, Inc.	25
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	28
Stamford Rubber Supply Company	22
Sun Oil Company, Sun Petroleum Products	(Opposite Title Page) 16
Superior Zinc Corporation	27
Thiokol Corporation, The	6
Titanium Pigment Corporation	29
United Carbon Company	(Inside Front Cover)
Vanderbilt, R. T. Company	19
Witco Chemical Company	2

Essential Reading for Rubber Men—

RUBBER:
Natural & Synthetic

By H. J. STERN

New text book on Production and Processing including Compounding Ingredients, Machinery and Methods for the Manufacture of various Rubber Products.

200 Illustrations—491 Pages

$12.00* Postpaid
(Sold Only in U.S. and Canada)

LATEX
IN INDUSTRY

By ROYCE J. NOBLE, Ph.D.

Second Edition of this well-known Text Book on Latex.

912 Pages—25 Chapters
Bibliography—Indexed

$15.00* Postpaid in U.S.
$16.00 All Other Countries

RUBBER RED BOOK

Directory of the Rubber Industry

Contains Complete Lists of Rubber Manufacturers and Suppliers of Materials and Equipment, Services, etc.

Tenth Issue—1955–56 Edition

$10.00* Postpaid

RUBBER AGE

The Industry's Outstanding Technical Journal Covering the Manufacture of Rubber and Rubberlike Plastics Products.

SUBSCRIPTION RATES

	U.S.	Canada	Other
1 Year	$5.00	$5.50	$6.00
2 Years	7.50	8.50	9.50
3 Years	10.00	11.50	13.00

Single copies (up to 3 months) 50¢
Single copies (over 3 months) 75¢

PALMERTON PUBLISHING CO., INC.
101 West 31st St., New York 1, N. Y.

(*) Add 3% Sales Tax for Copies to New York City Addresses

HIGH TEMPERATURE. Excellent performance and retention of flexibility at temperatures as high as 300°F. can be obtained with HYPALON products. Reports BL-262 and BL-267 discuss this subject.

OZONE. No HYPALON composition has ever been observed to crack in the presence of ozone. Report BL-269 tells this story.

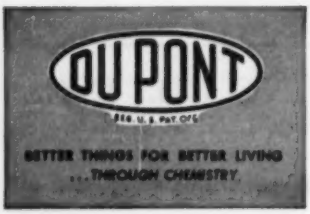
WEATHERING. Bright-colored and pastel-tinted as well as black compositions of HYPALON retain physical properties and appearance during long outdoor exposure. See Report BL-274 for more information.

OXIDIZING CHEMICALS. HYPALON compositions have great resistance to attack by oxidizing chemicals such as concentrated sulfuric acid and hypochlorite solutions. They perform well in a wide range of other chemicals and solvents. Performance indications and data are given in Reports BL-261 and BL-271.

And, in addition, HYPALON does not support combustion and resists deterioration by oil and grease.

The general story of HYPALON is given in Report No. 55-3

Ask our District Offices for the reference reports if you don't have them.



E. I. du Pont de Nemours & Co. (Inc.)
Elastomers Division

DISTRICT OFFICES:

Akron 8, Ohio, 40 East Buchtel Ave. at High Street . POrtage 2-8461
Atlanta, Ga., 1261 Spring St., N. W. . . . . EMerson 5391
Boston 10, Mass., 140 Federal St. . . . . HAncock 6-1711
Charlotte 2, N. C., 427 West Fourth St. . . . . CHarlotte 5-5561
Chicago 3, Ill., 7 South Dearborn St. . . . . ANdover 3-7000
Detroit 35, Mich., 13000 West 7-Mile Rd. . . . . UNiversity 4-1963
Houston 25, Texas, 1100 E. Holcombe Blvd. . . . . JAckson 8-1432
Los Angeles 58, Calif., 2930 E. 44th St. . . . . LOgan 5-6464
Trenton 8, N. J., 1750 North Olden Ave. . . . . EXport 3-7141
In Canada contact Du Pont Company of Canada Limited, Box 660, Montreal.

Material for ALL RUBBER and PLASTIC COMPOUNDING

COLORS

FILLERS

SOFTENERS

EXTENDERS

PLASTICIZERS

RESINS . . .
PARA-COUMARON INDENES
HYDRO-CARBON TERPENES
MODIFIED STYRENES
AROMATIC HYDRO-CARBONS

PRECISION Uniformity

You can depend upon the *Precision* character of Harwick Standard Chemicals regardless of the quantity requirement . . . Here is dependable assurance of uniformity in any type compounding material for rubber and plastics to give *certainty* in product development and production runs.

Our services are offered in co-operative research toward the application of any compounding material in our line to your production problems.

HARWICK STANDARD CHEMICAL CO.

AKRON 5, OHIO

BRANCHES: BOSTON, TRENTON, CHICAGO, LOS ANGELES

You can formulate *FASTER... BETTER* with

HORSE HEAD® ZINC OXIDES

FORMULATE FASTER!

...Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

FORMULATE BETTER!

...Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

...Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 38, N. Y.